

# Mineral Sources of Calcium and Phosphorus in Soils of the Northeastern United States

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Apatite is ubiquitous in igneous, metamorphic, and sedimentary rocks, although usually in trace amounts. Apatite is the primary source of P and, due to its relatively rapid dissolution rate, can be an important Ca source in noncarbonate soils. We investigated the distribution of apatite using a 1 mol L<sup>-1</sup> HNO<sub>3</sub> extraction of glacial till soils at 31 sites across the northeastern United States. Parent materials formed from crystalline silicate and clastic sedimentary rocks contained 0.2 to 41 mmol Ca kg<sup>-1</sup> soil and 1 to 27 mmol P kg<sup>-1</sup> soil; at most of these sites, the P/Ca ratio was approximately 3:5, indicating the dominance of apatite. Parent materials underlain by carbonate rocks had 3 to 16 mmol P kg<sup>-1</sup> soil, similar to the noncarbonate groups, but had large concentrations of easily weathered Ca (56–1890 mmol kg<sup>-1</sup> soil) due to the extraction of carbonates. The same extraction procedure applied to samples from the upper 30 cm of mineral soil at the same sites showed lower concentrations of both Ca and P than in the C horizon, except for a few sites where the upper soil layers probably developed in different parent materials than the current C horizon. We also measured neutral-salt-exchangeable Ca concentrations in the 10- to 20-cm depth increment. 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. For this reason, the exchangeable Ca concentration in the upper soil was correlated to the concentration of 1 mol L<sup>-1</sup> HNO<sub>3</sub> extractable Ca in the underlying soil parent material. To predict concentrations of apatite in parent materials and the concentrations of exchangeable Ca in overlying horizons in greater detail would require more specific characterization of bedrock sources.

Understanding mineral sources of Ca in soils of the northeastern United States is important because plant-available Ca has been leached from the soil at accelerated rates for several decades (Lawrence et al., 1999; Likens et al., 1998), possibly resulting in Ca limitation in some forest ecosystems (Horsley et al., 2000; Huntington, 2005; Long et al., 1997). Plagioclase,

the dominant Ca-bearing mineral in noncarbonate soils in the region, weathers too slowly to compensate for the Ca lost from the exchangeable pool (Likens et al., 1998; Nezat et al., 2004). Apatite, Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>(F,Cl,OH), although it is usually present only in trace amounts, may be an important mineral source of Ca because it dissolves several orders of magnitude more rapidly than plagioclase (Oxburgh et al., 1994; Valsami-Jones et al., 1998; Welch and Ullman, 1993). For example, at the Hubbard Brook Experimental Forest in New Hampshire, apatite represents <1% of the soil mineral mass (12% of total Ca) yet its dissolution is responsible for at least 20% of the Ca weathered from the soils since the area was deglaciated 14,000 yr ago (Nezat et al., 2004). In the Adirondack Mountains, apatite accounts for ~1 to 8% of the total Ca in some soil parent materials (Yanai et al., 2005).

Apatite is common in igneous, metamorphic, and sedimentary rocks. In igneous rocks, apatite is found in both plutonic and volcanic rocks ranging in chemical composition from

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felsic to ultramafic (Piccoli and Candela, 2002). In metamorphic rocks, apatite is found in pelitic, carbonate, basaltic, and ultramafic rocks of all metamorphic grades (Spear and Pyle, 2002). Apatite may appear as individual grains or as inclusions in aluminosilicate minerals such as feldspar and biotite. Apatite is also present in a variety of sedimentary rock types. In clastic rocks, both detrital and authigenic apatite have been found in rocks formed from continental and marine deposits (Bouch et al., 2002; Rasmussen, 1996; Roden-Tice and Tice, 2005). Apatite is also common in carbonate rocks, usually as carbonate-apatite,  $\text{Ca}_5(\text{PO}_4\text{CO}_3\text{OH})_3(\text{F},\text{Cl},\text{OH})$  (Knudsen and Gunter, 2002). Sedimentary rocks may also contain biological apatite such as bones and teeth (Kohn and Cerling, 2002).

Because apatite is easily weathered, the concentrations of apatite in soils are expected to be lower than in the underlying parent material. The depletion of apatite from soil during soil development has been documented in chronosequence studies (Crews et al., 1995; Schlesinger et al., 1998; Walker and Syers, 1976). This depletion of apatite from surface soils accompanied by its persistence at depth has also been documented in relatively young soils (Beck and Elsenbeer, 1999; Blum et al., 2002). In addition, depletion of apatite from surface soils during the initial stages of weathering has been interpreted from the presence of apatite in young detrital lake sediments (<5000 years old) following deglaciation and its absence in older lake sediments (Filippelli and Souch, 1999). Similarly, carbonate minerals weather very rapidly from soil profiles and are almost always depleted from surface horizons even in extremely young and poorly developed soils (Lichter, 1998; Vandenberg and Protz, 1995).

Although apatite is the most important primary mineral source of P and potentially an important source of Ca, it is not routinely measured in operationally defined plant-available pools. Exchangeable Ca extracted by a neutral salt solution (Hendershot et al., 1993; Robertson et al., 1999) is the most common index of Ca availability. Plant-available P is commonly quantified using anion-exchange resins or a  $0.5 \text{ mol L}^{-1}$   $\text{NaHCO}_3$  extraction (Hedley et al., 1982; Schlesinger et al., 1998). Neither of these methods assesses the amount of apatite susceptible to chemical weathering.

A new sequential extraction procedure allows apatite to be distinguished from more weathering-resistant aluminosilicate minerals in soils (Nezat et al., 2007). In recent studies, this procedure revealed that apatite was present in trace amounts in the lower B horizon and C horizon at the Hubbard Brook Experimental Forest in New Hampshire (Blum et al., 2002; Nezat et al., 2004) and at other sites in the northeastern United States underlain by granitoid bedrock (Yanai et al., 2005). The distribution of apatite in other soil parent materials across the northeastern United States is not well known.

The first objective of this study was to determine the concentration of Ca and P in easily weathered minerals in soil parent material at 31 sites with various bedrock lithologies across the northeastern United States. Based on our previously published sequential extraction method (Nezat et al., 2007), we defined easily weathered minerals as those that can be removed by a  $1 \text{ mol L}^{-1}$   $\text{HNO}_3$  solution. Using the chemical composition of the  $1 \text{ mol L}^{-1}$   $\text{HNO}_3$  extract, we inferred the concentration of apatite in the parent materials. We divided soil parent materials into three categories based on their underlying

bedrock type. Crystalline silicate rocks included noncarbonate igneous and metamorphic rocks such as gneiss, schist, and granitoid rocks. Clastic sedimentary rocks included shale, siltstone, and sandstone. Carbonate rocks included limestone and dolostone as well as carbonate rocks interlayered with clastic sedimentary rocks.

A comparison of a general geologic map (Fig. 1) and soil distributions in the northeastern United States (NRCS Web Soil Survey, [websoilsurvey.nrcs.usda.gov/app/](http://websoilsurvey.nrcs.usda.gov/app/), verified 3 Sept. 2008) shows that bedrock and soil order are roughly correlated in the northeastern United States. That is, Spodosols are common on glacial deposits of crystalline silicate bedrock, Inceptisols are prevalent on the Alleghany Plateau where clastic sedimentary rocks are the major rock type, and Alfisols are located in a narrow belt running east-west across New York where carbonate bedrocks are located. In this study, we limited some of the other variables that affect soil formation (i.e., climate, time for soil development, and topography) by choosing soils in a humid continental climate that have developed on glacial deposits of similar age (left by the last retreat of the Laurentide Ice Sheet) on relatively flat ground.

In addition to studying soil parent materials, we examined the occurrence of easily weathered sources of Ca and P in weathered soil horizons. In addition to apatite, some of the P and Ca present in organic matter or adsorbed to Al and Fe oxides would be included in this easily weathered fraction (Nezat et al., 2007). We expected to find that apatite was depleted from near-surface soils compared with the soil parent material or C horizon.

Finally, we tested for a relationship between the amount of easily weathered minerals (apatite and carbonate) in the underlying soil parent materials and the exchangeable Ca concentration of surface soil horizons. Although there are other variables that affect exchangeable Ca in soil, such as organic matter content and cation exchange capacity, we wanted to examine whether or not exchangeable Ca concentration could be predicted solely from bedrock type.

## MATERIALS AND METHODS

### Site Selection and Sampling

Thirty-one study sites were selected in New York, Pennsylvania, New Hampshire, and Maine to include a range of igneous, metamorphic, and sedimentary parent materials. In areas covered by ice sheets during the past 20,000 yr, which includes all of our study area, the soil parent materials are glacial deposits, mostly glacial till. Because the till generally represents the bedrock within an  $\sim 15$ -km radius in the direction from which the glacier advanced (Bailey et al., 2003; Crowl and Sevon, 1999; Isachsen et al., 2000), we selected sites for sampling based on the bedrock composition at and north of each site (Fig. 1, Table 1).

We selected 16 sites underlain by metamorphic and igneous bedrock in Maine, New Hampshire (White Mountains), and New York (Adirondack and Taconic Mountains). The sampling site in Maine, located in the Seaboard Lowland section of the New England Province, is underlain by granite (Osberg et al., 1985). The bedrock at the four sites in the White Mountains is gneiss, granite, and schist (Barton et al., 1997; Lyons et al., 1997). In New York, the Adirondack Mountains are composed primarily of granitoid rocks including charnockite, anorthosite, and mangerite but in the northwest region of the Adirondacks, marble, calcsilicate rock, and quartzite are also present

(Isachsen et al., 2000). The Taconic Mountains in southeastern New York are composed of schist and quartzite (Isachsen et al., 2000).

Fifteen of the study sites are underlain by sedimentary bedrock and are in the St. Lawrence Valley (northern New York), western New York, and northern Pennsylvania (Fig. 1). In New York, nine sites are underlain by limestone or dolostone, and five sites are underlain by clastic sedimentary rocks, i.e., sandstone, shale, or siltstone (Isachsen et al., 2000). At three sites in the St. Lawrence Valley, proglacial lake deposits lie over carbonate bedrock but are composed of noncarbonate sedimentary deposits; we reclassified these three sites as clastic sedimentary rock.

One soil pit at each of the sampling locations was excavated to the C horizon. At most of the sites, soil samples were collected from 0 to 10, 10 to 20, and 20 to 30 cm below the top of the mineral soil, and from the bottom of the soil pit in the C horizon. The soils collected from Hubbard Brook Experimental Forest were collected by horizon (Nezat et al., 2004).

## Sample Processing

All samples were dried at 105°C and sieved through a 2-mm screen. Soils were sequentially extracted (Nezat et al., 2007) to identify selected pools of Ca, Mg, and P. The exchangeable fraction was extracted by mixing ~0.5 g of soil with 5 mL of 1 mol L<sup>-1</sup> NH<sub>4</sub>Cl on a shaker table for ~18 h at room temperature. To dissolve apatite and carbonates, the residual material was then shaken with 1 mol L<sup>-1</sup> HNO<sub>3</sub> for 18 h at 10°C (Nezat et al., 2007). After each extraction, the mixture was centrifuged and the supernatant was collected and filtered through a 0.45-µm membrane. All 1 mol L<sup>-1</sup> NH<sub>4</sub>Cl and 1 mol L<sup>-1</sup> HNO<sub>3</sub> extracts were evaporated to dryness on a hot plate and redissolved in 5% HNO<sub>3</sub>.

Both the exchangeable and 1 mol L<sup>-1</sup> HNO<sub>3</sub> extractable fractions were then diluted with 2% HNO<sub>3</sub> and analyzed for Ca, Mg, and P concentrations on a PerkinElmer Optima 3300DV inductively coupled plasma–optical emission spectrometer (PerkinElmer, Norwalk, CT) using a five- to eight-point calibration curve. Analysis of a certified reference material (Soil Solution A, High Purity Standards, Charleston, SC) indicated an accuracy of ±5%.



Fig. 1. Location of samples collected in the northeastern United States.

To verify the presence of apatite and explore its relationship with other minerals in crystalline silicate soils, we examined six of the soil parent materials collected from the Adirondack Mountains, New York. Samples were sieved to obtain the 250- $\mu\text{m}$  to 2-mm size fraction. Subsamples of this fraction were impregnated with epoxy and prepared as polished thin sections. Minerals were identified using an energy dispersive spectrometer on a Hitachi S3200N scanning electron microscope (Hitachi High Technologies, Schaumburg, IL).

## Data Analysis

To test the null hypothesis that soil chemistry did not differ among bedrock types, a two-tailed Student's *t*-test, assuming equal variances, was performed on each pair. Because skewness and kurtosis values indicated that data were not normally distributed, data were log-transformed before statistical analysis in order to satisfy this requirement for the *t*-test. The equality of the variances of the groups was tested using an *F* test. Significance was tested at  $\alpha = 0.05$ .

## RESULTS

### Identification of Calcium- and Phosphorus-Bearing Minerals in Soil Parent Materials

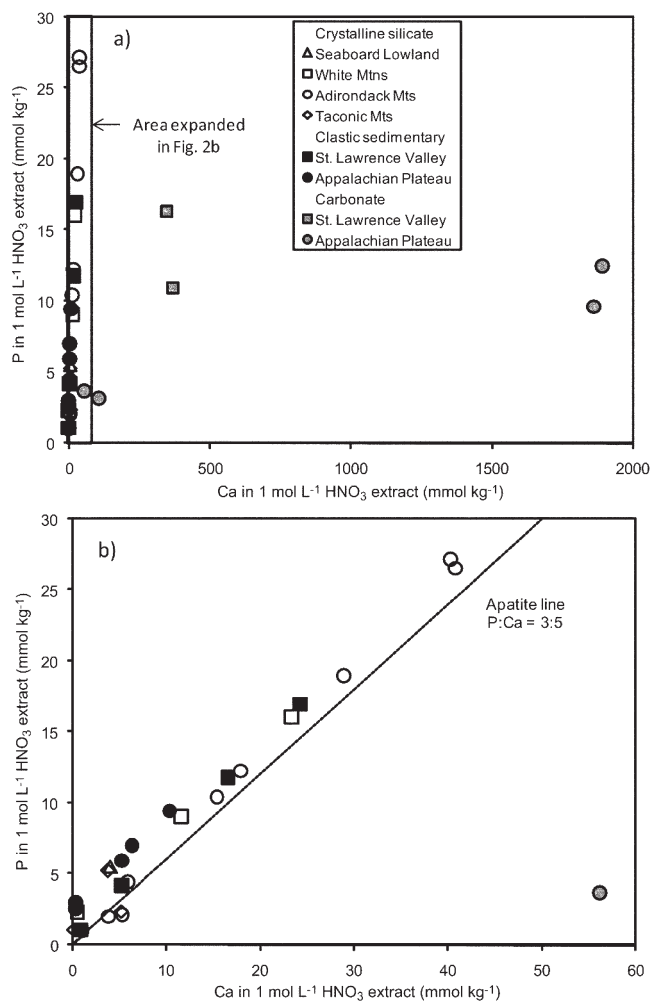
We used a 1 mol L<sup>-1</sup> HNO<sub>3</sub> extract of samples from 31 sites to determine which soil parent materials in the northeastern United States contained apatite (Fig. 2). Because this extract dissolves apatite congruently (Nezat et al., 2007), soil parent materials containing apatite as the primary source of easily weathered Ca and P should have a P/Ca ratio of 3:5, the stoichiometric ratio in apatite.

Most of the soil parent material derived from crystalline silicate rocks had a P/Ca ratio in the 1 mol L<sup>-1</sup> HNO<sub>3</sub> extract close to 3:5 (Fig. 2b). Calcium concentrations ranged from 0.2 to 41 mmol kg<sup>-1</sup> soil and P ranged from 1.1 to 27 mmol kg<sup>-1</sup> soil, indicating that these soil parent materials varied widely in apatite concentration (0.002–0.4% apatite in soil by weight based on Ca concentrations). These soil parent materials did not differ systematically by region. For example,

**Table 1. Sampling locations in the northeastern United States. The bedrock at each site includes bedrock found up to 10 km northward. The surficial deposits are glacial till at all sites except for Brasher Falls (northwest), Fort Jackson, and Southville, which have proglacial lake deposits.**

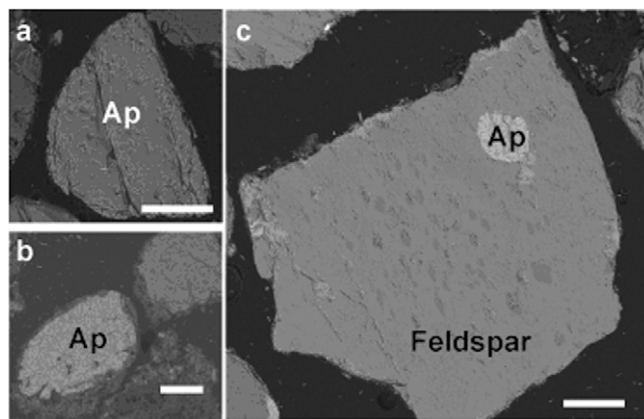
Location	State		Latitude	Longitude	Bedrock
Crystalline silicate bedrock					
Osborn	ME	Seaboard Lowland	44°48'	68°16'	alkali feldspar granite
Iron Mountain (T30)	NH	White Mtns.	44°9'	71°14'	pelitic schist
Bartlett Exp. Forest (H1)	NH	White Mtns.	44°3'	71°17'	granite, syenite
Sabbaday Falls (M6)	NH	White Mtns.	44°0'	71°25'	granite, syenite
Hubbard Brook Exp. Forest	NH	White Mtns.	43°57'	71°43'	granodiorite, pelitic schist
Hopkinton	NY	Adirondack Mtns.	44°31'	74°36'	charnockite, granitic and quartz syenite gneiss
Altamont	NY	Adirondack Mtns.	44°16'	74°27'	mangerite, syenite gneiss, charnockite, metasedimentary rock, granitic gneiss
Sand Pond	NY	Adirondack Mtns.	43°57'	73°54'	metanorthosite, anorthositic gneiss
Wolf Pond	NY	Adirondack Mtns.	43°54'	74°21'	charnockite, granitic and quartz syenite gneiss
Old Squaw	NY	Adirondack Mtns.	43°44'	74°22'	gabbroic metanorthosite, anorthositic gneiss, mangerite to charnockitic gneiss
Day	NY	Adirondack Mtns.	43°20'	74°3'	biotite and hornblende granitic gneiss, metasedimentary rock, migmatite
Black River	NY	Adirondack Mtns.	43°34'	74°51'	metasedimentary rock, granitic gneiss, marble
Ferris Lake	NY	Adirondack Mtns.	43°24'	74°42'	metasedimentary rock, granitic gneiss
Lafayetteville	NY	Taconic Mtns.	41°58'	73°43'	slate, phyllite, schist, dolostone, sandstone
Stissing Mt.	NY	Taconic Mtns.	41°56'	73°41'	slate, phyllite, schist
Wassaic	NY	Taconic Mtns.	41°47'	73°34'	slate, phyllite, schist, marble
Sedimentary bedrock (clastic)					
Brasher Falls (northwest)	NY	St. Lawrence Valley	44°52'	74°50'	limestone, dolostone
Fort Jackson	NY	St. Lawrence Valley	44°43'	74°45'	dolostone, sandstone, siltstone
Southville	NY	St. Lawrence Valley	44°41'	74°51'	dolostone, sandstone, siltstone
CH 201	NY	Alleghany Plateau	42°38'	76°24'	shale
CH 342	NY	Alleghany Plateau	43°30'	75°58'	sandstone, shale
Happy Valley	NY	Alleghany Plateau	43°27'	76°2'	sandstone, siltstone, shale
Klondike	NY	Alleghany Plateau	43°22'	75°59'	sandstone, shale
Swift Hill	NY	Alleghany Plateau	42°27'	78°14'	shale and siltstone
Tioga State Forest, Gleason	PA	Alleghany Plateau	41°39'	76°56'	sandstone
Sedimentary bedrock (carbonate)					
Brasher Falls (southeast)	NY	St. Lawrence Valley	44°51'	74°39'	limestone, dolostone
Grantville	NY	St. Lawrence Valley	44°51'	74°55'	limestone, dolostone
Black Pond	NY	Alleghany Plateau	43°47'	76°12'	limestone, shale
CH 392	NY	Alleghany Plateau	43°11'	76°41'	limestone, dolostone
CH 379	NY	Alleghany Plateau	43°1'	76°22'	limestone, dolostone
Rush	NY	Alleghany Plateau	42°58'	77°40'	limestone, dolostone





**Fig. 2.** Phosphorus vs. Ca from a 1 mol L<sup>-1</sup> HNO<sub>3</sub> extraction (at 10 °C) of C horizon samples from across the northeastern United States: (a) all data—not surprisingly, carbonate-rich sites have the highest Ca concentrations; (b) an enlarged view at low Ca concentrations. Many of the parent materials derived from crystalline silicate and clastic sedimentary rocks fall near the dashed line, which represents the P/Ca ratio of apatite (3:5).

the Adirondacks had sites with the highest and some of the lowest apatite concentrations. Some of the soils derived from crystalline silicate rocks (Osborn, Stissing Mountain, Sabbaday



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

Falls, and Lafayetteville) had P/Ca > 3:5, suggesting the presence of other P sources in addition to apatite.

Soils collected from clastic sedimentary sites (located on the Appalachian Plateau) generally had Ca and P concentrations that were not significantly different from the crystalline-silicate soils ( $P = 0.22$  for Ca and 0.80 for P); however, the P/Ca ratio was typically >3:5 (Fig. 2b), suggesting other sources of P besides apatite.

Three sites in the St. Lawrence Valley (Brasher Falls northwest, Fort Jackson, and Southville) overlie carbonate bedrock, but are in an area where carbonate-poor glacial lake deposits blanket glacial till. The lack of abundant Ca in the 1 mol L<sup>-1</sup> HNO<sub>3</sub> extract and the P/Ca ratio of 3:5 is consistent with the origin of these three soil parent materials as siliclastic glacial lake deposits rather than carbonate-rich glacial till. Field textural analysis confirmed that these soil parent materials were composed of well-sorted sand, which also indicates that they are lakeshore deposits and not glacial till.

Soil parent materials underlain by carbonate bedrock had significantly higher Ca concentrations in the 1 mol L<sup>-1</sup> HNO<sub>3</sub> extract than soils derived from crystalline silicate and clastic sedimentary rocks ( $P < 0.001$ ; Fig. 2a). These sites also had high concentrations of 1 mol L<sup>-1</sup> HNO<sub>3</sub> extractable Mg (252–344 mmol Mg kg<sup>-1</sup> soil) relative to other sites (<75 mmol Mg kg<sup>-1</sup> soil), suggesting the presence of dolomite or high-Mg calcite. Phosphorus was present in these materials at concentrations that did not differ significantly from those at the noncarbonate sites ( $P > 0.33$ ).

To investigate the relationship between apatite and silicate minerals in granitoid parent materials, we examined thin sections of soil parent materials from the Adirondack Mountains. We found apatite either as individual grains (Fig. 3a), partially included in silicate minerals (Fig. 3b), or completely included in silicate minerals (Fig. 3c). Apatite grains ranged from 50 to 300 μm in diameter.

We examined bedrock type as an explanation of the regional pattern in available (1 mol L<sup>-1</sup> HNO<sub>3</sub> extractable) Ca in soil parent material (Fig. 4). It is clear from the map that the highest Ca availability is located near carbonate bedrock. As described above, however, three of the five sites in the St. Lawrence Valley overlying carbonate bedrock did not contain any evidence of carbonates.

### Easily Extracted Calcium and Phosphorus in Upper Soil Profiles

We determined the 1 mol L<sup>-1</sup> HNO<sub>3</sub> extractable Ca and P in the upper soil profile (Fig. 5). Not surprisingly, carbonate-dominated soils generally had higher Ca concentrations than the soils overlying crystalline silicate or clastic sedimentary bedrock. Generally, the Ca and P concentrations were lower in the surface soils than the parent materials (Fig. 2), as expected due to apatite weathering, plant uptake, and leaching. Notable exceptions were Lafayetteville, a crystalline silicate bedrock site in which the Ca in the 0- to 10-cm sample was three times that in the C horizon, and Swift Hill (clastic sedimentary) and Black Pond (carbonate), in which the P was 16 and five times, respectively, in surface horizons what it was in the C horizon. These sites are probably cases where the C horizon is not representative of the parent material for the upper portion of the profile. Three additional sites had more modest excesses (up to threefold) of P concentrations in this extract in the surface

soils compared with the C horizon: H1, CH 201, and Stissing Mountain. Excluding these six sites, the concentration of Ca in the surface soils (averaging up to three layers per site) as a fraction of the concentration in the C horizon was 28% (13 crystalline silicate sites), 22% (four clastic sedimentary sites), and 14% (eight carbonate sites). For P, these fractions were 35% (crystalline silicates), 25% (clastic sedimentary sites), and 41% (carbonates). The difference between the retention of Ca and P was not significant ( $P > 0.4$  in paired  $t$ -tests) except in the case of the carbonate sites ( $P = 0.03$ ).

### Relationship between Exchangeable Calcium in Upper Soils and Soil Parent Material

We tested the dependence of soil Ca availability on the type of parent material by comparing the exchangeable Ca concentration at the 10- to 20-cm depth to the Ca in the 1 mol L<sup>-1</sup> HNO<sub>3</sub> extract of the respective soil parent material (Fig. 6). Not surprisingly, soils formed on carbonate-dominated soils had the highest exchangeable Ca concentrations, whereas soils formed on clastic sedimentary and crystalline silicate rocks had

approximately an order of magnitude less exchangeable Ca. The exchangeable Ca at 10 to 20 cm was correlated with the easily extracted Ca in the 1 mol L<sup>-1</sup> HNO<sub>3</sub> extract of the soil parent material ( $P < 0.001$ ,  $r^2 = 0.52$ ). This pattern, however, was driven by the high Ca concentrations in the carbonate soils. When the carbonate sites were omitted from the analysis, there was no significant relationship ( $P = 0.56$ ,  $r^2 = 0.01$ ).

## DISCUSSION

### Apatite in soil parent materials

The importance of apatite in young soils at the Hubbard Brook Experimental Forest in New Hampshire has previously been reported (Blum et al., 2002; Nezat et al., 2004; Yanai et al., 2005). Because apatite is common in crystalline silicate rocks, we predicted that soil parent materials in other young soils in the northeastern United States that were derived from crystalline silicate rocks would also contain apatite. We identified apatite in most of these soil parent materials based on the similarity between the P/Ca ratio in the 1 mol L<sup>-1</sup> HNO<sub>3</sub> extract and that in apatite (3:5) (Fig. 2b). Some of the soils derived from crystalline silicate rocks (Osborn, Stissing

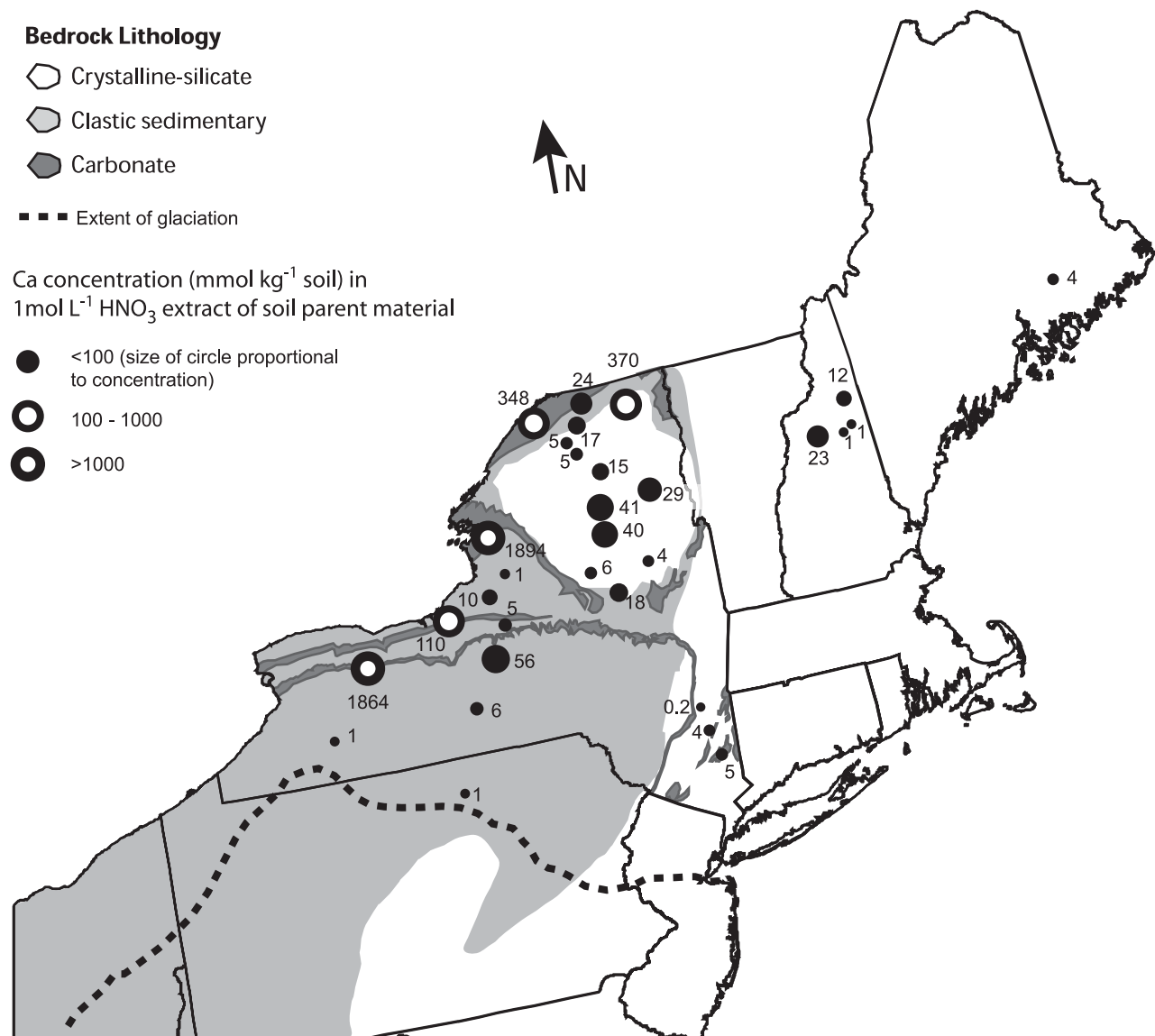
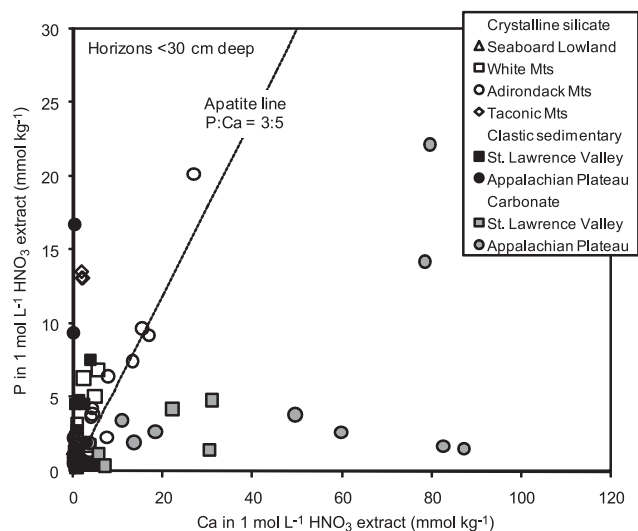


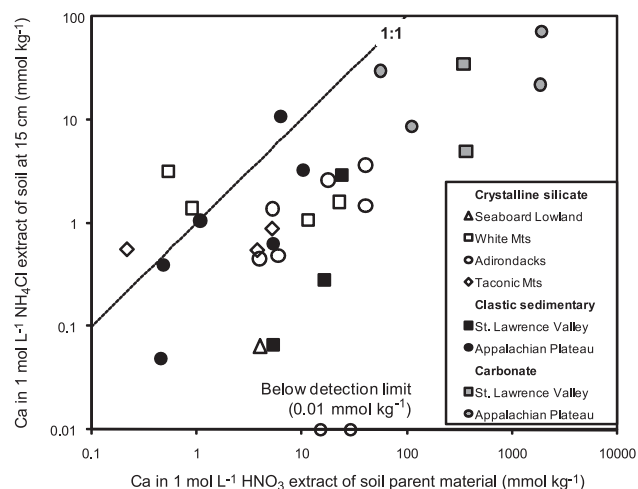
Fig. 4. Calcium concentration in 1 mol L<sup>-1</sup> HNO<sub>3</sub> extract of soil parent materials.



**Fig. 5. Phosphorus vs. Ca from a 1 mol L<sup>-1</sup> HNO<sub>3</sub> extraction (at 10 °C) of surface soils (<30 cm deep) from across the northeastern United States. Each site is represented by two to three samples collected roughly at 5, 15, and 25 cm.**

Mountain, Sabbaday Falls, and Lafayetteville) had P/Ca ratios >3:5, suggesting the presence of other P sources in addition to apatite. In fact, the 1 mol L<sup>-1</sup> HNO<sub>3</sub> solution also extracts Ca and P from organic matter and weathering products such as P adsorbed to Al and Fe oxides (Nezat et al., 2007), which are typically a negligible fraction of soil parent materials derived from crystalline silicate rocks. Monazite, another primary phosphate mineral found in crystalline silicate rocks, is less common than apatite and is not likely to be extracted by a 1 mol L<sup>-1</sup> HNO<sub>3</sub> solution (Nezat et al., 2007).

In addition to its presence in igneous and metamorphic rocks, apatite is also found in a variety of sedimentary rocks as detrital, authigenic, or biological apatite (Bouch et al., 2002; Knudsen and Gunter, 2002; Rasmussen, 1996). Although Ca and P were present in the 1 mol L<sup>-1</sup> HNO<sub>3</sub> extract of most of the soil parent materials derived from the sedimentary rocks, the P/Ca ratio for most of these samples was >3:5, indicating other sources of P in addition to apatite. In the region we studied, young soils developed from crystalline silicate and clastic



**Fig. 6. Calcium concentration of a 1 mol L<sup>-1</sup> NH<sub>4</sub>Cl extract of soil at 10- to 20-cm depth vs. Ca concentration of a 1 mol L<sup>-1</sup> HNO<sub>3</sub> extract of soil parent material. The dashed line represents a 1:1 ratio.**

(noncarbonate) sedimentary rocks have similar ranges of easily weathered Ca and P (Fig. 2b).

Carbonate rocks also contain apatite, often as carbonate-apatite (Knudsen and Gunter, 2002). Because the 1 mol L<sup>-1</sup> HNO<sub>3</sub> extract also dissolves calcite, we used the P concentration to estimate the concentration of apatite in these soil parent materials. Although carbonate-rich soil parent materials contain considerably more 1 mol L<sup>-1</sup> HNO<sub>3</sub> extractable Ca, the concentration of easily weathered P in carbonate parent materials is similar to that found in crystalline silicate and clastic sedimentary parent materials (Fig. 2a).

The concentration of apatite estimated from the Ca and P concentrations in the 1 mol L<sup>-1</sup> HNO<sub>3</sub> extract may be less than the total because some apatite may occur as inclusions in, and may be completely armored by, weathering-resistant minerals such as biotite, plagioclase, and K feldspar, which are not dissolved by this extract (Nezat et al., 2007). Unlike apatite inclusions, apatite that is present as free grains or partially included in silicate minerals may be exposed to the soil solution and release nutrients during weathering. At the Hubbard Brook Experiment Forest, 70% of the total P in the soil parent materials was removed by the 1 mol L<sup>-1</sup> HNO<sub>3</sub> extract (Nezat et al., 2004), indicating that the remaining 30% was from apatite inclusions and other P-bearing minerals such as monazite. In the current study, a range of 10 to 100% of the total P was removed by the 1 mol L<sup>-1</sup> HNO<sub>3</sub> extract from the soil parent materials (data not shown) with no pattern among bedrock type or geographic region. While this extraction method quantifies the amount of apatite that is currently exposed to soil solution, biological, chemical, and physical processes are continually occurring in soils and may expose more apatite with time. For example, this method does not account for apatite inclusions that may be accessed by mycorrhizal fungi as they tunnel through silicate minerals (Jongmans et al., 1997; Landeweert et al., 2001). To determine total apatite using this extraction method, soils should be pulverized before extraction. In this study, we extracted untreated soils because we were interested in apatite currently susceptible to weathering.

### Easily Weathered Minerals in the Upper Soil Profile

Although apatite is present in soil parent materials, it can be weathered from surface soils in a few thousand years due to its rapid weathering rate (Crews et al., 1995). Assuming that the original composition of surface soils was similar to the soil parent material and that inputs from atmospheric dust have been minor, apatite concentrations in the soil should increase with depth due to the decrease in weathering (Schlesinger et al., 1998). At the Hubbard Brook Experimental Forest, apatite was identified in lower B horizons (Blum et al., 2002), suggesting that apatite has not been completely weathered at this depth.

As apatite weathers, P accumulates in organic matter or binds to Al and Fe oxides (Crews et al., 1995; Schlesinger et al., 1998; Walker and Syers, 1976). The 1 mol L<sup>-1</sup> HNO<sub>3</sub> solution releases Ca and P from both of these pools as well as from apatite (Nezat et al., 2007), making it difficult to estimate the concentration of apatite present in these soil horizons. The portion of P concentration loss we report (two-thirds in crystalline silicates and three-quarters in clastic sedimentary sites) should be a conservative estimate of the portion of apatite weathered, both because of the weathering products appearing in this



operationally defined pool and also because of the loss of other elements from the profile. The concentration of an immobile element as an indicator of mass loss, combined with identification of apatite crystals, could give a more exact measure of apatite loss. It has been suggested that P may be more tightly retained than Ca in surface horizons due to high ecosystem demand relative to its lithologic supply (Jobbágy and Jackson, 2001); however, we did not find a greater fraction of Ca than P lost from the upper part of the profile, relative to the C horizon, except in the carbonate sites.

### Effect of Soil Parent Material on the Exchangeable Fraction

The relationship we found between easily weathered Ca in parent materials and exchangeable Ca in soils is informative because it may give a first-order approach to identifying soils that have high exchangeable Ca concentrations. Where the composition of the bedrock is well known, it would be very appealing to use a bedrock map to predict the area most susceptible to Ca depletion and soil acidification. There are some limitations to this approach, however. First, the surficial geology also needs to be considered. Although glacial till is typically derived from local bedrock, other glacial deposits are not. For example, glacial lake deposits located in the St. Lawrence Valley (at Brasher Falls northwest, Southville, and Fort Jackson) are carbonate poor despite the fact that they are underlain by calcareous bedrock. In nearby soils that are underlain by the same bedrock but developed on glacial till (e.g., Brasher Falls southeast and Grantville), carbonates are present. Second, it is important to keep in mind that there is a wide variation in parent material composition within the broad categories of crystalline silicate and clastic sedimentary rocks, which influences soil mineral and chemical composition (Fig. 2). To predict the availability of Ca and P to vegetation and the susceptibility of soils to acidification at specific sites would require detailed characterization of the glacial till composition (Bailey and Hornbeck, 1992; Hornbeck et al., 1997), along with an evaluation of the soil's capacity to retain exchangeable Ca.

### CONCLUSIONS

Using a new sequential extraction method, we quantified the concentration of "easily weathered" Ca and P pools, such as apatite and carbonate, in soil parent materials derived from a variety of bedrock types. The similarity between the P/Ca ratio in apatite and the 1 mol L<sup>-1</sup> HNO<sub>3</sub> extract indicates that apatite is the dominant source of P and Ca in this easily weathered pool in most soil parent materials derived from crystalline silicate rocks. This method also distinguishes the apatite that is exposed to soil solution from that which is completely armored by weathering-resistant silicate minerals and thus not currently susceptible to weathering.

Although known as the dominant P-bearing primary mineral in soil, apatite has not been studied as a source of Ca in soils until recently. In this study, we have shown that apatite is present in many parent materials of young soils in the northeastern United States where Ca depletion is a concern. Previous methods of characterizing soil Ca and P do not routinely identify the apatite fraction. Although usually present in trace amounts, apatite dissolves orders of magnitude more rapidly than plagioclase, the dominant Ca-bearing silicate mineral in many soils. To predict changes in plant-available

Ca concentrations in soil in response to acid deposition and forest harvesting, it is important to be able to quantify this Ca pool.

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