

# Substantial biologically mediated phosphorus depletion from the surface of a Middle Cambrian paleosol

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## ABSTRACT

Despite recent work, a comprehensive understanding of pre-Devonian terrestrial ecosystems remains elusive, resulting in frequent speculation about their composition. Terrestrial microbial mats are known from the Precambrian paleosol record, and bryophytes are known from the Middle Ordovician palynological record. The intervening time, however, remains enigmatic, although recent studies indicate a progressive “greening” of the Precambrian prior to the first unambiguous fossil evidence for land plants. In this study, an older than 503 Ma, heavily weathered, clay-rich soil was identified and provides a window to a probable Cambrian terrestrial landscape. The paleosol developed on the ancient continent of Laurentia in a dry, subtropical climate. Mobilization of Si, Al, and P indicate the influence of organic acids. Apatite, a recalcitrant mineral present throughout the majority of the weathered section, is notably absent from the top 30 cm of the paleosol. Few secondary phosphates and a complete absence of oxide- or carbonate-bound P indicate that once biologically weathered, P remained in an ecosystem-available form during the lifetime of this paleosol. The zone of apatite dissolution coincides with intense argillan development, indicating clay flocculation in the presence of soil solutions rich in labile Ca<sup>2+</sup>. Enhanced P weathering coupled with high Ca<sup>2+</sup> concentrations as a result of in situ apatite dissolution is a biosignature previously linked to the activities of mycorrhizal fungi. Biosignatures of mycorrhizal fungi in a Middle Cambrian paleosol add further evidence to the notion that there was an important terrestrial fungal presence prior to the first unequivocal evidence for terrestrial land plants.

## INTRODUCTION

Molecular-clock and geochemical studies suggest that terrestrial ecosystems are of considerable antiquity, with terrestrial bacteria present as early as the Archean (Watanabe et al., 2000; Battistuzzi et al., 2004; Battistuzzi and Hedges, 2009; Driese et al., 2011) and fungi and land plants present potentially as early as the Neoproterozoic (Heckman et al., 2001). These results are at odds with a majority of the fossil record. To date, carbon and oxygen isotope geochemistry (Horodyski and Knauth, 1994; Knauth and Kennedy, 2009), biotic enhancement of element mobility (Neaman et al., 2005a, 2005b, 2006), and changes in phosphorus mobility during the Proterozoic and Phanerozoic (Driese et al., 2007) have hinted at a systematic “greening” of the terrestrial landscape during the Neoproterozoic and Cambrian. The Cambrian may have been a critical turning point for the development of Phanerozoic terrestrial ecosystems, with the emergence of cryptospores of putative bryophytes (Strother et al., 2004). Studies of Proterozoic and Cambrian paleosol geochemistry, particularly of the fate of apatite, may help illuminate changes in terrestrial flora that are not otherwise recorded in the fossil record, and may aid in resolving the discrepancy between molecular-clock predic-

tions and observations from the fossil record. In this study, the geochemistry and micromorphology of a Middle Cambrian paleosol from Elk Point, South Dakota, United States, revealed mobilization of Si and Fe, a signature of organic acid influence, as well as intense dissolution of apatite, a P-rich mineral, from the surface environment coupled with development of illuvial clay features (likely a result of soil solutions rich in labile Ca<sup>2+</sup> as a result of apatite dissolution), a pattern that has been previously linked to the P-uptake activities of mycorrhizal fungi.

## MATERIALS AND METHODOLOGY

The Elk Point core was drilled south of Elk Point, South Dakota (NW NW NE Sec. 13, T90N R50W; see Fig. DR1 in the GSA Data Repository<sup>1</sup>). The basement material in this core is a strongly foliated 1.733 ± 0.002 Ga metagabbro (McCormick and Hammond, 2004). The weathered section can be visually divided into two distinct zones: a paleosaprolite with

metagabbro textures (1.6 m) overlain by a red paleosol where metagabbro textures have been destroyed (3 m). The overlying Mount Simon Sandstone (McCormick, 2005) contains a basal conglomerate enriched in pyrite. The age of the generally unfossiliferous Mount Simon Sandstone was constrained to older than 503 Ma, based on *Cedaria*, *Crepicephalus*, and *Aphelaspis* faunal zones present in higher formations (Shergold and Cooper, 2004; McCormick, 2005; Runkel et al., 2007). The pyritization of the upper layers of the paleosol indicates a soft sediment at burial, placing its likely time of formation in the Middle Cambrian.

Core description and sampling were completed at the South Dakota Geological Survey core repository in Vermillion, South Dakota. Subsequent work was completed at Pennsylvania State University. Exterior surfaces from the core were removed prior to grinding to 100 mesh (149 μm). Major oxides were determined for bulk samples using a Perkin-Elmer Optima 5300 inductively coupled plasma-atomic emission spectrometer (ICP-AES). Core material was sent to National Petrographic Service for thin-section preparation. Cut surfaces and thin sections were used for quantitative X-ray mapping of elemental distributions on a Horiba XGT-500. Mineralogy was determined using X-ray diffraction (XRD) on a Rigaku D-MAX RAPID microdiffractometer with three-dimensional image plate. Each powdered sample was packed into a 0.7 mm quartz tube and scanned for 3 min. MDI Jade was used to determine likely mineralogy.

Enrichment and depletion trends for major oxides were calculated using the soil element-mass-transfer equation (Brimhall and Dietrich, 1987; Anderson et al., 2002), which compares the mass of mobile oxides to an immobile oxide. The immobile element used in many paleosol studies, including this one, is Al (Rye and Holland, 2000; Driese et al., 2007), although Ti is also commonly used (see Fig. DR2 for normalization of the Elk Point paleosol to Ti). The deepest metagabbro sample at 3096 cm below the soil surface was used as the reference for comparisons.

Normative mineral analysis was used to determine partitioning of oxides in minerals determined by XRD. Oxide weight percents were converted to mole proportions. S and Fe

<sup>1</sup>GSA Data Repository item 2012147, Tables DR1 and DR2 (raw oxide results and normative mineral analysis results), and Figures DR1–DR3 (map of study area, Elk Point element-mass-transfer normalized to Ti, and apatite dissolution imagery), is available online at [www.geosociety.org/pubs/ft2012.htm](http://www.geosociety.org/pubs/ft2012.htm), or on request from [editing@geosociety.org](mailto:editing@geosociety.org) or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

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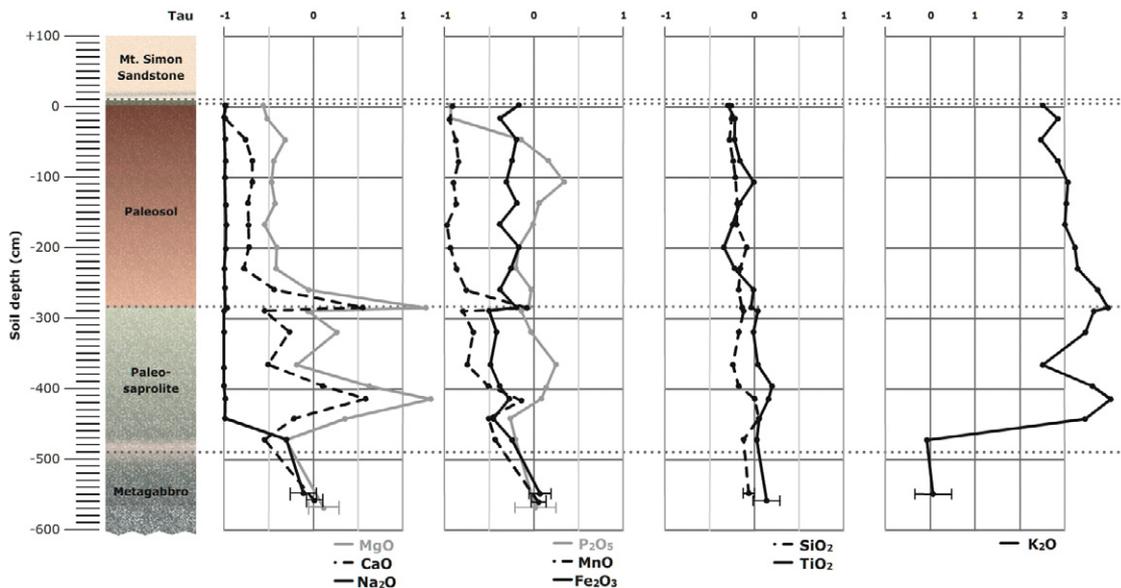


Figure 1. Oxide enrichment and depletion for the Elk Point core (South Dakota, United States), normalized to Al. Tau values were calculated using soil element-mass-transfer equations (Brimhall and Dietrich, 1987; Anderson et al., 2002), where  $-1$  indicates 100% loss and  $+1$  indicates 100% enrichment. Bottommost point is an aggregate of all metagabbro data ( $n = 8$ ). The deepest sample at 3096 cm below the soil surface was used as the reference for comparisons.

were attributed to pyrite, with remaining Fe attributed to hematite. P and Ca were attributed to apatite (and hematite-associated P, if necessary). Remaining Ca and Mg were attributed to dolomite (and calcite, if necessary). Al, K, and Si were attributed to illite. Remaining Si was attributed to quartz. Ti was attributed to titanium oxides. The main purpose of the normative mineral analysis was to determine partitioning of P in soil minerals.

## RESULTS

The core section can be visibly divided into four zones, starting with a quartz-dominant sandstone with basal conglomerate rich in pyrite that penetrates into the upper few centimeters of the paleosol surface. Paleosol mineralogy (hematite and illite) is present down to 286 cm below the paleosol surface. Paleosaprolite mineralogy (dolomite, illite, and hematite) is present 286–480 cm below the paleosol surface. Below 480 cm, metagabbro mineralogy dominates (albite, anorthite, ilmenite, and grunerite).

Oxide enrichment and depletion patterns are detailed in Figure 1. ICP-AES results (Table DR1 in the Data Repository) show substantial depletion of soluble cations, including complete loss of Na, substantial (50%–90%) loss of Ca, Mg, and Mn, and moderate (20%–50%) loss of Fe. Ca and Mg are moderately to significantly (10%–130%) enriched in the paleosaprolite. K is substantially (200%–400%) enriched throughout the profile. Si is somewhat (10%–25%) depleted, with the depletion increasing up-section. P is somewhat (10%–25%) depleted, with a few zones of enrichment (<35%) throughout the weathered section, and is significantly depleted (92%–97%) in the top 30 cm.

Soil micromorphological features are visible in thin section. Clay translocation is read-

ily identifiable and is most noticeable near the surface, where illuvial clay structures (argillans) are present between 13 and 37 cm below the surface of the paleosol and dominate the soil microfabric at 28 cm (Fig. 2A). Dolomite is visible within the base of the paleosol as individual rhombs and throughout the paleosaprolite as larger amalgamations of rhombs and grains (Fig. 2C). The unweathered metagabbro

consists of plagioclase, biotite, and hornblende, and their textures visually persist into the paleosaprolite despite complete chemical alteration. They degrade substantially up-section (particularly biotite via delamination) and are replaced by clays in the paleosol. There is no visual evidence for allochthonous material in the weathered horizon, nor do Si and Ti contents indicate substantial introduction of such material.

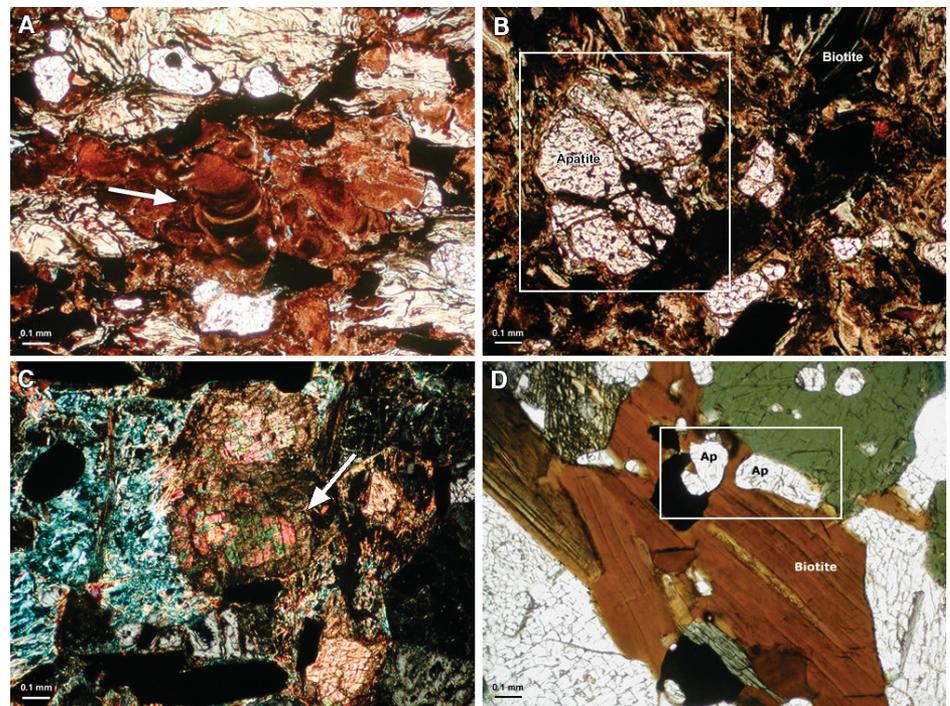


Figure 2. Major features in the Elk Point paleosol (South Dakota, United States). A: A laminated argillan indicative of downward clay mobilization (–16 cm). B: Heavily degraded apatite grain near the top of paleosol (–46 cm), showing fracturing and infilling of fractures by iron oxide and clay. C: Dolomite grains in the paleosaprolite, showing replacement and secondary overgrowth (–316 cm). D: Apatite grains associated with biotite in the unweathered metagabbro (–1576 cm).

Normative mineral analysis results (Table DR2) suggest apatite content ranging between 2.2 and 4.9 wt% (average 3.4 wt%). All P can be accounted for in apatite, indicating no oxide- or carbonate-bound P. These results are consistent with X-ray maps of thin sections, which show P exclusively associated with Ca in apatite grains.

Apatite is present throughout the metagabbro, frequently in close association with biotite (Fig. 2D). Moving up-section into the weathered zone, biotite becomes intensely altered while apatite remains minimally altered, with some fractured grains present farther up-section. Intense degradation of apatite is not observed until 30 cm depth (Fig. 2B). Fragments tend to be smaller and more rounded and appear to have been subject to heavy alteration, resulting in fracturing and infilling of cracks by clays and iron oxides, as compared to intact grains in the metagabbro (see Fig. DR3 for more imagery). Apatite abruptly disappears above this zone and is completely absent in the top 30 cm. There is little evidence of widespread secondary phosphate precipitation. Biotite, which is intensely altered throughout the weathered section, shows no visible changes in its weathered state through the depths where apatite is altered.

## DISCUSSION

### Subtropical Weathering

The substantial loss of mobile cations in the Elk Point paleosol is consistent with pedogenesis (Driese et al., 2007; Zhang et al., 2007). In drier environments, carbonate can precipitate at the average depth of wetting (Retallack, 2001). In this profile, carbonates appear at the base of the paleosol and throughout the underlying paleosaprolite (>260 cm depth). However, their dominant form is dolomite, which is not typical of soil environments. Coupled with substantial K enrichment throughout the profile, it is likely that dolomitizing metasomatic fluids, which commonly affect paleosols in the Midcontinent region (Liu et al., 2003; Driese et al., 2007), dolomitized pre-existing pedogenic carbonates and illitized probable relict smectites. The geochemistry of the paleoweathered zone is otherwise unaffected, an observation supported by previous studies of weathering in the Midcontinent region (Driese et al., 2007). Surficial pyrite enrichment penetrates a few centimeters into the paleosol and is likely the result of early diagenesis of the soft Fe-rich paleosol surface by S-rich oceanic waters.

Paleosol development at Elk Point is similar to modern weathering on mafic parent material (Schaetzl and Anderson, 2005). A P-poor leaching zone (not quite an eluvial horizon due to the persistence of clay) is present above an illuvial clay-rich horizon that grades to a cambic horizon. The paleosol overlies a carbonate-rich

paleosaprolite and indicates significant weathering in a subtropical climate. The presence of carbonates at depth and a lack of evidence for significant Al mobilization suggest a dry environment (Neaman et al., 2005a).

### Apatite Dissolution and Fate of Phosphorous

The primary inorganic source of P in terrestrial environments is weathering from apatite, and so P tends to be a limiting nutrient over geologic time. P can be liberated from apatite by abiotic dissolution, dissolution in the presence of organic acids, or targeted biological attacks.

Modern soils forming in acidic conditions tend to show substantial mobilization of Al and development of quartz-rich eluvial horizons. Acidic soil conditions also favor the destruction of smectite clays and formation of kaolinite (Schaetzl and Anderson, 2005). There is no evidence for kaolinite clays, eluvial horizon development, or substantial mobilization of Al, indicating that the Elk Point soil was likely alkaline during its lifetime. Apatite is relatively weathering-resistant in alkaline soils (Taunton et al., 2000b; Welch et al., 2002; Neaman et al., 2005b), thus precluding a purely abiotic explanation for P losses.

Si, Fe, and P have been mobilized in the weathered section, showing moderate losses throughout the profile (with near-complete loss of P from the surface). Enhanced mobilization of these elements during pedogenesis has been experimentally verified to be a result of organic ligand activity (Neaman et al., 2005a, 2005b). Previous researchers have also attributed P loss from Precambrian soils to the presence of organic acids (Driese et al., 2007, 2011).

Targeted attacks on minerals have been previously reported for mycorrhizal fungi (Ness and Vlek, 2000; Bonneville et al., 2009). Hallmarks of a mycorrhizal attack on apatite include removal of P from soil solution via uptake, with concomitant increase in  $\text{Ca}^{2+}$  near the dissolving apatite crystal (Ness and Vlek, 2000). Argillans are a very prominent component of the soil fabric just above the last appearance of apatite. In modern soils, clays disperse in horizons that are depleted in cations, and flocculate in zones that are either prone to desiccation or rich in cations such as Ca and Mg (Schaetzl and Anderson, 2005). Pedogenic carbonates (later dolomitized) present well below the argillan-rich zone indicate that desiccation was not limited to the top 30 cm of this paleosol. The ubiquity of clay coatings and argillans near the zone of intense apatite degradation is consistent with flocculation in a zone where the soil solution would have been persistently enriched in  $\text{Ca}^{2+}$  as a result of active apatite dissolution.

Once liberated from apatite, P can be lost to runoff or leaching, remain in biologically available organic (organic P) and inorganic

(secondary phosphates) forms, or precipitate with Fe- and Al-oxides (Crews et al., 1995). The presence of carbonates at depth and a lack of Al mobilization preclude inorganic leaching from the paleosol as an explanation for loss of P. Bacteria and fungal hyphae suppress secondary phosphate precipitation through uptake of P or active dissolution of previously precipitated secondary phosphates (Taunton et al., 2000a). The paucity of secondary phosphates at Elk Point, combined with a complete absence of Fe- or Al-oxide-bound P, indicate that P remained in a bioavailable form as a result of the activities of soil denizens during the lifetime of this paleosol. In the absence of secondary phosphate precipitation, apparent P enrichment at depth is likely an artifact of recalcitrant apatite grains becoming concentrated as more labile components of the paleosol were lost.

## CONCLUSIONS

Molecular-clock and equivocal palynological studies consistently suggest that fungal and bryophyte ecosystems are older than previously established (Middle Ordovician). In addition, the mobilization of P, a limiting nutrient on land, from ancient soil surface horizons appears to have intensified from the Precambrian to the Cambrian (Driese et al., 2007; Driese and Medaris, 2008; Horodyskyj, 2009). Taken together, these various lines of evidence suggest the increasing prominence of bryophytes and their associated rhizospheres at the expense of lichens and microbial mats that would have previously occupied the terrestrial realm during the Neoproterozoic and Cambrian. The Middle Cambrian Elk Point paleosol utilized in this study recorded a geochemical footprint of terrestrial biota during this time of transition. Although moderately altered by postburial metasomatism, the paleosol preserves clear geochemical and pedogenic signals indicating a targeted biological attack on the P-rich mineral apatite in the top 30 cm of the profile during weathering in a dry, subtropical climate. Paleosol geochemistry is inconsistent with a purely abiological mechanism for apatite loss in the top 30 cm of the paleosol. P loss via thorough leaching or P retention in soil reservoirs such as oxides or secondary phosphate precipitates is likewise not supported by the geochemical evidence, indicating that P remained in a bioavailable form once liberated from apatite. Additionally, illuvial clay dominates the soil microfabric in the transition zone between apatite-rich and apatite-depleted soil. Clay flocculation is enhanced in zones of high soil cation concentrations, which would have been present in a zone of active apatite dissolution.

The substantial depth of dissolution (30 cm), combined with preferential uptake of P over Ca (resulting in high soil  $\text{Ca}^{2+}$  concentrations

as evidenced by argillan formation), is strongly indicative of the presence of mycorrhizal fungi in this Middle Cambrian U.S. Midcontinent soil. Mycorrhizal fungi typically colonize vascular plant roots, but can also form mycorrhizal-like associations with bryophytes (Read et al., 2000; Renzaglia et al., 2007). Mycorrhizal fungi are known from fossils as old as 460 Ma (Redecker et al., 2000) and likely evolved earlier. The geochemical signatures of mycorrhizal fungi in this Middle Cambrian paleosol push back their first appearance by >43 m.y., and cast a new light on the players involved in terrestrial ecosystem reorganization during this enigmatic period of time.

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#### REFERENCES CITED

- Anderson, S.P., Dietrich, W.E., and Brimhall, G.H., 2002, Weathering profiles, mass-balance analysis, and rates of solution loss: Linkages between weathering and erosion in a small, steep catchment: *Geological Society of America Bulletin*, v. 114, p. 1143–1158.
- Battistuzzi, F.U., and Hedges, S.B., 2009, A major clade of prokaryotes with ancient adaptations to life on land: *Molecular Biology and Evolution*, v. 26, p. 335–343, doi:10.1093/molbev/msn247.
- Battistuzzi, F.U., Feijao, A., and Hedges, S.B., 2004, A genomic timescale of prokaryote evolution: Insights into the origin of methanogenesis, phototrophy, and the colonization of land: *BMC Evolutionary Biology*, v. 4, p. 44, doi:10.1186/1471-2148-4-44.
- Bonneville, S., Smits, M.M., Brown, A., Harrington, J., Leake, J.R., Brydson, R., and Benning, L.G., 2009, Plant-driven fungal weathering: Early stages of mineral alteration at the nanometer scale: *Geology*, v. 37, p. 615–618, doi:10.1130/G25699A.1.
- Brimhall, G.H., and Dietrich, W.E., 1987, Constitutive mass balance relations between chemical composition, volume, density, porosity, and strain in metasomatic hydrochemical systems: Results on weathering and pedogenesis: *Geochimica et Cosmochimica Acta*, v. 51, p. 567–587, doi:10.1016/0016-7037(87)90070-6.
- Crews, T.E., Kitayama, K., Fownes, J.H., Riley, R.H., Herbert, D.A., Mueller-Dombois, D., and Vitousek, P.M., 1995, Changes in soil phosphorus fractions and ecosystem dynamics across a long chronosequence in Hawaii: *Ecology*, v. 76, p. 1407–1424, doi:10.2307/1938144.
- Driese, S.G., and Medaris, L.G., 2008, Evidence for biological and hydrological controls on the development of a Paleoproterozoic paleoweathering profile in the Baraboo Range, Wisconsin, USA: *Journal of Sedimentary Research*, v. 78, p. 443–457, doi:10.2110/jsr.2008.051.
- Driese, S.G., Medaris, L.G., Ren, M., Runkel, A.C., and Langford, R.P., 2007, Differentiating pedogenesis from diagenesis in early terrestrial paleoweathering surfaces formed on granitic composition parent materials: *Journal of Geology*, v. 115, p. 387–406, doi:10.1086/518048.
- Driese, S.G., Jirsa, M.A., Ren, M., Brantley, S.L., Sheldon, N.D., Parker, D., and Schmitz, M., 2011, Neoproterozoic paleoweathering of tonalite and metabasalt: Implications for reconstructions of 2.69 Ga early terrestrial ecosystems and paleoatmospheric chemistry: *Precambrian Research*, v. 189, p. 1–17, doi:10.1016/j.precamres.2011.04.003.
- Heckman, D.S., Geiser, D.M., Eidell, B.R., Stauffer, R.L., Kardos, N.L., and Hedges, S.B., 2001, Molecular evidence for the early colonization of land by fungi and plants: *Science*, v. 293, p. 1129–1133, doi:10.1126/science.1061457.
- Horodyski, R.J., and Knauth, L.P., 1994, Life on land in the Precambrian: *Science*, v. 263, p. 494–498, doi:10.1126/science.263.5146.494.
- Horodyski, L.B., 2009, Soil formation and terrestrial biosignatures in the Middle Cambrian [Ph.D. thesis]: College Park, Pennsylvania State University, 139 p.
- Knauth, L.P., and Kennedy, M.J., 2009, The late Precambrian greening of the Earth: *Nature*, v. 460, p. 728–732.
- Liu, J., Hay, R.L., Deino, A., and Kyser, T.K., 2003, Age and origin of authigenic K-feldspar in uppermost Precambrian rocks in the North American Midcontinent: *Geological Society of America Bulletin*, v. 115, p. 422–433, doi:10.1130/0016-7606(2003)115<0422:AAOAK>2.0.CO;2.
- McCormick, K.A., 2005, Drilling of an aeromagnetic anomaly in southeastern South Dakota: Results from analysis of Paleozoic and Precambrian core: *South Dakota Geological Survey Report of Investigations*, 119, 19 p.
- McCormick, K.A., and Hammond, R.H., 2004, Geology of Lincoln and Union Counties, South Dakota: *South Dakota Geological Survey Bulletin*, v. 39, 43 p.
- Neaman, A., Chorover, J., and Brantley, S.L., 2005a, Element mobility patterns record organic ligands in soils on early Earth: *Geology*, v. 33, p. 117–120, doi:10.1130/G20687.1.
- Neaman, A., Chorover, J., and Brantley, S.L., 2005b, Implications of the evolution of organic acid moieties for basalt weathering over geological time: *American Journal of Science*, v. 305, p. 147–185, doi:10.2475/ajs.305.2.147.
- Neaman, A., Chorover, J., and Brantley, S.L., 2006, Effects of organic ligands on granite dissolution in batch experiments at pH 6: *American Journal of Science*, v. 306, p. 451–473, doi:10.2475/06.2006.03.
- Ness, R.L.L., and Vlek, P.L.G., 2000, Mechanism of calcium and phosphate release from hydroxyapatite by mycorrhizal hyphae: *Soil Science Society of America Journal*, v. 64, p. 949–955, doi:10.2136/sssaj2000.643949x.
- Read, D.J., Duckett, J.G., Francis, R., Ligrone, R., and Russell, A., 2000, Symbiotic fungal associations in 'lower' land plants: *Royal Society of London Philosophical Transactions*, ser. B, v. 355, p. 815–831, doi:10.1098/rstb.2000.0617.
- Redecker, D., Kodner, R., and Graham, L.E., 2000, Glomalean fungi from the Ordovician: *Science*, v. 289, p. 1920–1921, doi:10.1126/science.289.5486.1920.
- Renzaglia, K.S., Schuette, S., Duff, R.J., Ligrone, R., Shaw, A.J., Mishler, B.D., and Duckett, J.G., 2007, Bryophyte phylogeny: Advancing the molecular and morphological frontiers: *The Bryologist*, v. 110, p. 179–213, doi:10.1639/0007-2745(2007)110[179:BPATMA]2.0.CO;2.
- Retallack, G.J., 2001, *Soils of the past: An introduction to paleopedology*: Oxford, Blackwell Science, 404 p.
- Runkel, A.C., Miller, J.F., McKay, R.M., Palmer, A.R., and Taylor, J.F., 2007, High-resolution sequence stratigraphy of lower Paleozoic sheet sandstones in central North America: The role of special conditions of cratonic interiors in development of stratal architecture: *Geological Society of America Bulletin*, v. 119, p. 860–881, doi:10.1130/B26117.1.
- Rye, R., and Holland, H.D., 2000, Geology and geochemistry of paleosols developed on the Hekpoort Basalt, Pretoria Group, South Africa: *American Journal of Science*, v. 300, p. 85–141, doi:10.2475/ajs.300.2.85.
- Schaetzl, R.J., and Anderson, S., 2005, *Soils: Genesis and geomorphology*: Cambridge, UK, Cambridge University Press, 817 p.
- Shergold, J.H., and Cooper, R.A., 2004, The Cambrian period, in *Gradstein, F.M., et al., eds., A geologic time scale 2004*: Cambridge, UK, Cambridge University Press, p. 147–164.
- Strother, P.K., Wood, G., Taylor, W., and Beck, J., 2004, Middle Cambrian cryptospores and the origin of land plants: *Memoirs of the Association of Australasian Palaeontologists*, v. 29, p. 99–113.
- Taunton, A.E., Welch, S.A., and Banfield, J.F., 2000a, Geomicrobiological controls on light rare earth element, Y and Ba distributions during granite weathering and soil formation: *Journal of Alloys and Compounds*, v. 303–304, p. 30–36, doi:10.1016/S0925-8388(00)00597-1.
- Taunton, A.E., Welch, S.A., and Banfield, J.F., 2000b, Microbial controls on phosphate and lanthanide distributions during granite weathering and soil formation: *Chemical Geology*, v. 169, p. 371–382, doi:10.1016/S0009-2541(00)00215-1.
- Watanabe, Y., Martini, J.E.J., and Ohmoto, H., 2000, Geochemical evidence for terrestrial ecosystems 2.6 billion years ago: *Nature*, v. 408, p. 574–578, doi:10.1038/35046052.
- Welch, S.A., Taunton, A.E., and Banfield, J.F., 2002, Effect of microorganisms and microbial metabolites on apatite dissolution: *Geomicrobiology Journal*, v. 19, p. 343–367, doi:10.1080/01490450290098414.
- Zhang, G.-L., Pan, J.-H., Huang, C.-M., and Gong, Z.-T., 2007, Geochemical features of a soil chronosequence developed on basalt in Hainan Island, China: *Revista Mexicana de Ciencias Geológicas*, v. 24, p. 261–269.

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