Evaluation of Bigby Cannon Limestone's Contributions to Pedogenesis Using Element Mass Flux Calculations

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KEYWORDS. chemical weathering, mass flux, Bigby Cannon Limestone

BRIEF. Bigby Cannon Limestone was analyzed to see if it contributes to soil development in Middle Tennessee.

ABSTRACT. Soil is the foundation of civilization. Soil development is an important process as it relates to agricultural practices, water quality, natural disasters, and construction uses, to name a few. Despite its importance, knowledge of how soil forms in Middle Tennessee is rather limited. Soil can be residual (formed from chemical weathering of bedrock) or transported (such as loess or alluvial sediments). This study aimed to better understand the parent material of a previously identified soil horizon found directly atop an outcrop of the Hermitage Formation. Results from previous analyses conducted on the soil and the Hermitage Formation hinted that weathering of the Hermitage was not the only contributor to the formation of the soil. Assuming that soil is primarily formed through weathering of bedrock, the new hypothesis proposed that weathering of the Bigby Cannon limestone formation, which is found directly above the Hermitage formation on the rock strata, also contributed to soil formation. Laser Ablation Inductively Coupled Plasma Spectrometry (LA-ICP-MS) analysis was done on the Bigby Cannon rock sample to determine the trace element fingerprints. Measured element concentrations and soil and rock densities were used to estimate element mass fluxes during chemical weathering. Results indicate it was possible for the Hermitage or the Bigby Cannon to have been the sole parent material, or a combination of both bedrocks could have contributed to the soil.

INTRODUCTION.

The study of sustainable soils is essential to protecting and improving various aspects of civilization [1]. Soil plays a vital role in the ecosystem, from supporting forests and grasslands to determining the quality of water. Nutrient depletion from soil can affect development of rainforests, and distribution of vegetation [2, 3]. Despite the numerous ramifications that result from understanding soil formation, little is known about the provenance of soil in Middle Tennessee. Therefore, this study sought to gain a better understanding of how soil develops in this area—its focus being on the Central Basin, a region well known for its rich soil. The Central Basin covers roughly 11,600 km^2 and has the Ordovician Hermitage and Bigby Cannon limestone formations exposed. Weathering of pure limestone cannot form soil, and studies have confirmed that soil found atop pure limestone formations are formed from aeolian parent material, such as African dust [4]. However, limestone in Tennessee is not pure, colloquially referred to as "dirty" limestone as it contains a high proportion of silt [5]. Therefore a possible source of soil in Middle Tennessee could be the weathering of bedrock. The soil could also originate from weathering of alluvial sediments, which are clay, silt, or gravel often carried and deposited by rushing streams, or weathering of loess, which is windblown glacial dust, or a combination of any of these end members.

As a part of an ongoing investigation, the soil was previously analyzed with similar methods used in this research and the Hermitage limestone was analyzed for general chemical composition (Katsiaficas and Ayers, pers. comm.). The results showed that the soil had much higher concentrations of the elements strontium, calcium, and most notably phosphorus, which was nearly five hundred times the amount found in Hermitage. With such great differences, this data insinuated that another source was contributing to the soil. The Bigby Cannon Limestone had previously been noted for its abundance of phosphate deposits [5]. Along with this information and its proximity to the soil, Bigby Cannon became the next suspect.

This study tested the hypothesis that weathering of the Bigby Cannon limestone contributed to pedogenesis (soil development). The collected Bigby Cannon sample and the already processed Hermitage sample were fused into two separate glass beads and mounted in epoxy. The beads were analyzed on the LA-ICP-MS (Laser Ablation Inductively Coupled Plasma Mass Spectrometer) and EDS (Electron Dispersive Spectroscopy) on the SEM (Scanning Electron Microscope) for elemental compositions. These apparatuses work together to completely break apart the molecules present in a sample using a high temperature plasma ion source, then counts the number of ions at a certain mass of the element, giving us information on elemental concentrations. This data, along with the measured bulk densities of both rocks, were used to calculate mass fluxes of the two bedrocks. Mass flux calculations estimate the changes in volume that occur in weathering by assuming the element zirconium is immobile in rock and soil [6,7].

MATERIALS AND METHODS.

Gathering the Bigby Cannon Sample.

To first locate the desired field site, the program ArcGIS, which compiles geologic information of an area onto a map, was used to find an outcrop near highway 840-W, less than a kilometer away from the previous outcrop where the soil and the Hermitage were collected and examined. The close proximity also reduced the number of confounding variables in the study, since the two bedrocks and the soil were exposed to nearly the exact same environmental conditions. A few kilograms of the bedrock were collected using a 4 lb sledgehammer and a chisel, carefully observing the physical characteristics of the rocks to ensure a representative sample. In the lab, some of the fist-sized pieces of Bigby Cannon limestone were massed and their density was calculated using volume displacement, which would be necessary for mass flux calculations later on. The majority of the collected rock samples were broken into smaller chunks with the sledge and put through the jaw crusher to obtain gravel-sized rock pieces.

Creating and Mounting the Bead.

About 200 grams of the crushed sample were pulverized in a shatterbox. Of this pulverized sample, about 10 grams of the fine powder were heated at 1000 °C for 30 minutes to remove carbonate, water and organic carbon. 0.5 grams of the heated sample was combined with 1.0 gram of $LiBO_2$ and ground thoroughly using mortar and pestle under acetone to create a homogeneous mixture. After letting the mixture dry, roughly 0.15 grams were heated in a graphite crucible at 1100 °C for 5 minutes to fuse into a small bead. This bead was then mounted in a 1" epoxy mount and polished. The Hermitage sample was also fused in to a glass bead, mounted, and polished using the same protocol.

Analyzing the Chemical Compositions.

Bulk composition of insoluble material was analyzed from both beads. Using the LA-ICP-MS and SEM, the concentrations of major elements and homogeneity of the bead were determined. The data was then processed using a computer program called Glitter! and converted onto an Excel spread sheet for mass flux calculations.

RESULTS.

Elemental Compositions.

The data from LA-ICP-MS analyses were imported into Excel and graphed based on atomic masses of the elements measured in each of the bedrock samples and the previously analyzed soil sample.

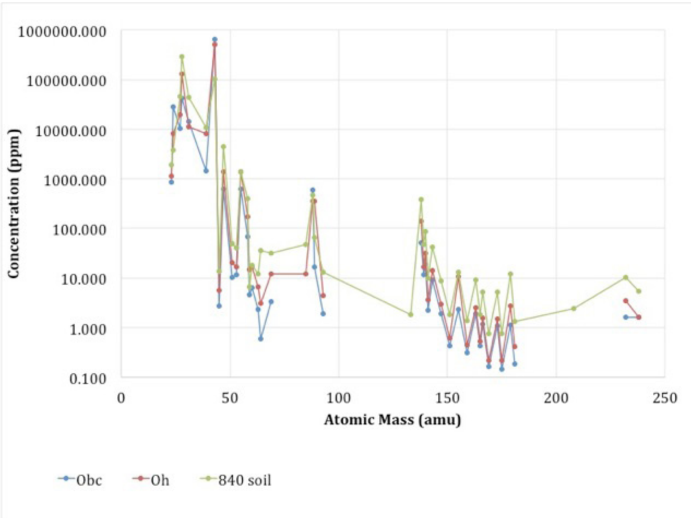

Figure 1. The graph shows how the soil, Bigby Cannon (Obc), and Hermitage (Oh) have very similar chemical compositions.

Mass Flux Calculations.

The volume strain due to dissolution of limestone to form soil was calculated from measured soil and bedrock densities and concentrations of zirconium, which was assumed to be immobile during weathering (Eq. 1). These equations show strain (ε) and mass flux per unit parent material volume (δ) during pedogenesis [7]. In these equations, j = major element of interest, w = weathered soil horizons, p = parent material, ρ = dry bulk density, C = concentration (weight %), and V = volume [6].

$$\varepsilon_{Zr,w} = \frac{(V_w - V_p)}{V_p} = \frac{\rho_p C_{Zr,p}}{\rho_w C_{Zr,w}} - 1 \quad (1)$$

The mass of each element that was added or removed during soil formation per unit volume δ was calculated from Eq. 2 for each of the limestone formations. Negative mass fluxes indicated that the element was leached out of the rock, likely contributing to the soil. Positive mass fluxes indicate that the element was gained from an additional source [7].

$$\delta_{j,w} = \frac{\rho_w C_{j,w}\left(\varepsilon_{Zr,w} + 1\right) - \rho_p C_{j,p}}{100} \quad (2)$$

Mass flux calculations were graphed based on the atomic masses of the elements.

DISCUSSION.

The soil and the Hermitage and Bigby Cannon limestones show a similar trend in their elemental concentrations, with the heavier elements tending to concentrate more in the soil. The mass flux data indicate the soil most likely resulted from chemical weathering rather than from transported materials. Therefore, Bigby Cannon remains the most likely contributor to the soil.

To gain more quantitative data of each rock's contributions, age spectra can be determined through zircon U-Pb geochronology. This is an exciting endeavor, as zircon has not been analyzed in limestone previously. This will also provide additional information on the efficiency and accuracy of zircon U-Pb dating for identifying source materials for soils. Zircon (ZrSiO4) is a prevalent mineral relatively resistant to extreme temperature and geologic processes. The lengthy process of sonication, high-density liquid separation, magnetic separation, and acid cleaning can isolate zircon grains. We can use lead and uranium isotopes from the zircon to measure ages. If U-Pb ages of zircon from the soil don't match those from zircon in the underlying bedrock, we would have to consider analyzing possible transported materials such as loess or alluvium. If they do match, we'll be able to get proportions of residues from Hermitage and Bigby Cannon that make up the soil.

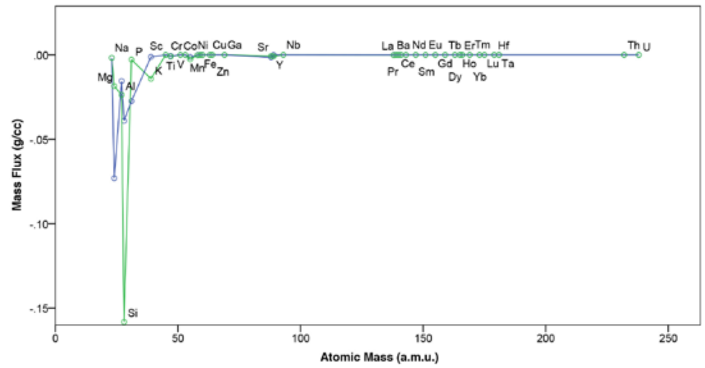

Figure 2. All of the elements for both the Hermitage (green) and the Bigby Cannon (blue) show negative mass fluxes. The absence of positive mass fluxes suggests that it is possible for the Hermitage or the Bigby Cannon to have been the sole parent material, or a combination of both bedrocks could have contributed to the soil.

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SUPPORTING INFORMATION.

Supplemental Methods.

Figure S1. Concentrations of Major Elements

Figure S2. Mass Fluxes for Obc and Oh

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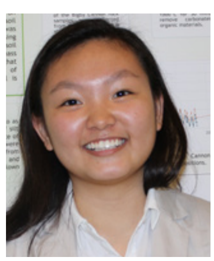

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