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THE CONTRIBUTION OF CLIMBING PLANTS TO SURFACE ACIDITY AND BIOPITTING EVIDENT AT THE UNIVERSITY OF OXFORD BOTANIC GARDEN, UK

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ABSTRACT: Fieldwork was executed at the University of Oxford Botanic Garden located in central Oxford, UK in order to examine enlarged holes on the surface of a c. 380-year-old border wall comprised of Headington stone. There are bee hotels located in the walled section within the Garden, where it is thought that red mason bees are responsible for the holes. Manual counts of the holes, however, revealed no clear spatial trend of an increasing frequency closer to the bee hotels. Supplementary research was conducted in order to ascertain the cause of these noticeable masonry holes. A digital pH meter was employed on-site with runoff collection of distilled water to measure surface acidity, which could be responsible for initial pitting on these limestone walls that could then be exploited (and enlarged) by bees. However, these large holes, measuring up to 23.41 mm across, could not be the product of environmental acidity alone, as due to organic acids released by (climbing) plants also found in this area. This multivariate problem is considered from all biological angles, including consideration of the influence of acidity due to vegetation (climbing plants) and the influence of bees. Both may be required for the establishment of these weathering features and their enlargement to holes. Even though it is known that bees are capable of removing sand grains to enlarge concavities in walls, they are not known to bore through limestone, which is considered to be a relatively hard stone.

KEYWORDS: Limestone; bioweathering; pitting; pH; English ivy; solitary (red mason) bees.

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1. INTRODUCTION: Biological weathering (bioweathering) examines the influence of flora and fauna on the in situ breakdown of rock. This type of weathering has both physical and chemical components that have been recognized in the literature. Keller and Frederickson (1), for instance, wrote an early paper on the impact of plants (and colloidal acids) on the weathering of rocks. These authors argued that plants accelerate rock weathering due to H-ion (H^+) and metal-ion (Ca, Mg, K, etc.) exchange extracted by roots. Chemical weathering is limited not only by water availability for wetting, but also where algae, moss, lichens, and other plants appear on rock surfaces. Plant rootlets are acid in reaction, because they are negatively charged (similar to organic and inorganic colloids), and surrounded by cations, mostly H-ions. These H-ions are chemically aggressive because they have chemical potential energy due to their high electrical charge that enables them to diffuse into openings at the crystal boundary. The high concentration of H-ions surrounding roots has consequences for the weathering of minerals, such as feldspars. Indeed, the roots of plants in lower stages of evolution carry a higher concentration of H-ions and, for instance, use up more K. H-ions can displace Na and Ca (e.g., Ca^{++}, K^+, and Na^+) and cause the displaced cation to be adsorbed by the root and, because they are assimilated by the plant, effectively removed from the chemical system. The build up of metallic cations as well as soluble silica gels and insoluble silica fragments can slow down weathering, with soluble silica dissolved and migrated towards the surface, forming a hard crust upon drying. Roots are capable of penetrating these surface layers comprising weathered residues. Acidity is affected by H-ions from clays, organic, and inorganic acids and can be removed if precipitated in an insoluble form or used (in metabolic processes) by plants. The rate of weathering is also affected by climatic conditions, such as atmospheric pressure and temperature range. A high weathering rate depends on the continued transfer and removal of metal cations (e.g., of Ca, Mg, K, etc.) from clay colloids (coatings appearing above the mineral surface) and H-ions are returned by plants through the roots (this is well depicted in (1), Fig. 2, p. 603). The removal of carbonates or biocarbonates of metal cations, as through carbonic acid naturally occurring in rainfall, leads to further weathering. Broken surfaces expose Ca^{++} and CO_3^{--} ions, with the latter group being especially vulnerable to H-ion attack due to its small and already highly charged carbon ion in combination with large oxygen ions. It is broken down because of the greater bond between O and H than between O and C. Metal cations (such as Ca) that are not assimilated by plants are precipitated as an insoluble mineral. Because acids are made available to rocks through water, carbonic acid, acid clay, acid humus, complex organic substances, and plant root systems, they should be considered as a critical part of bioweathering, including the latter (plants), whose role has been claimed to be bioprotective by some authors in recent years, for example (2-4).

In a paper by Winkler (5), various weathering agents were considered for building and monumental stone. These included atmospheric components, such as carbon dioxide, sulphates, chlorides, nitrates, smog, and rainwater (containing carbon dioxide), streams, soft waters, aggressive waters, lakes, seawaters and saline lakes, groundwater, and (lastly) plants and animals. Specifically, of plants and animals, lichens and mosses, animal activity, boring in carbonate rocks, borers in soft rock, and borers in hard rock and concrete were addressed. Lichens and mosses were considered for their mechanical water retention capacity as well as ion exchange and secretion of acids. The author observed that acidic (low pH) conditions are produced by lichen rhizoms and the roots of higher plants, including climbing vines of Boston ivy (*Parthenocissus tricuspidata*) and Virginia creeper (*Parthenocissus quinquefolia*), causing metal anion exchange, which is important for the breakup of carbonates. He also relays earlier research on the production of citric and oxalic acid from fungal cultures (of Fungi *Aspergillum niger*, *Spicaria* sp., and *Penicillium* sp.), the latter being the most active.

More recent studies have shown that plants do assimilate mineral/ rock substrates in their tissues. One study, for instance, observed increased concentrations of trace elements, such as Sr, in foliage of plants capable of accessing basalt and granite grains (6). Another study focusing on Hawaiian basalts weathered by lichens and higher plants observed chemical attack by bulk dissolution (7). Crustose lichens sampled in this study fragmented and chemically weathered rock and retained the material in the thallus. Higher plants, in particular, produced extensive chemical alteration (over unvegetated and lichen-encrusted samples), with fine plant roots appearing in the deeper zones of alteration. Zones of maximum dissolution were located particularly beneath roots, but associated microorganisms (e.g. fungi and bacteria) were also implicated in chemical weathering. The authors stated that roots serve an important function in vascular plants in the take up of water and nutrients, and are thereby involved in the chemical breakdown of material. Fungi and bacteria produce organic acids (chelating agents) that promote chemical weathering. Moreover, transpiration leads to the uptake of solutions by fine roots in plants. Other work on basaltic rock, in western Iceland, revealed that two to five times more Ca^{2+} and Mg^{2+} were released to streams in vegetated areas than in barren areas (8). These authors provided a summary that they compiled from various studies on the reasons for the role of rooted vascular plants in the acceleration of rock weathering: 1) rootlets and associated symbionts secrete organic acids and chelates, attacking minerals and releasing nutrient cations; 2) organic matter decay produces organic acids and carbonic acid; 3) evaportranspiration increases rainfall; and 4) plants anchor clay-rich soil against erosion and allow for the retention of water and weathering. Mottershead and colleagues (9) were able to identify etch features associated with plant roots on marble surfaces, with weathering concentrated at junctions in the root network (rather than at tips).

Some authors have focused on the impacts of air pollution, as from traffic, and vibrations. Nord and Holenyi (10) examined iron, sulfur, phosphorus, and chlorine as surface concentrations associated with traffic and stone decay. They, however, did acknowledge the complexity of the problem in that many natural sources are also responsible for stone weathering (e.g. soiling and pitting), including climatic conditions and microorganisms. For instance, humidity can augment the dissolution of calcite by water. Moreover, Török (11) observed discoloration by leaching, but also dissolution pitting and flaking on rainwashed ornamental stone (travertine) surfaces in Budapest, Hungary. Nord and Holenyi (10) did not, however, consider microorganisms and plants in the weathering process. Black colonies of *T. umbrina*, for instance, were found on surface micropits, which were created by *Trentepohlia*, on limestone monuments at the Mayan site of Edzna in Campeche, Mexico (12). Since there was no evidence of algal filaments, however, the damage was attributed to acids (metabolites). Pits (along with disintegration, scaling, exfoliation, and honeycomb weathering features) are also known to form in salty environments due to salt weathering (13).

Organic acids released by plant roots in the exchange of metal cations with rock surfaces in chemical weathering reduce the pH of rocks, leading to the dissolution of insoluble phosphates and rocks, including extrusive igneous, marble, and limestone (14). Thermo- halo-, and drought-tolerant bacteria, in particular, released useful minerals, such as P, K, Mg, Mn, Fe, Cu, and Zn. The authors reviewed the literature attributing bioweathering to microorganisms that colonize plant roots in addition to organic acids that roots exude. In addition to microorganisms, vascular plants are known to have weathered phosphorus from rocks since their evolution from ~420 Ma in the Devonian period some 400-360 Ma (15). According to this author, vascular plants amplify weathering rates an order of magnitude in comparison with lichens and mosses. Specifically, they are known for weathering Ca^{2+} and Mg^{2+} by factors of 10 and 18, respectively. Higher plants need to be considered in the chemical weathering (dissolution) of rocks, such as Brazilian basalt, as sources of major nutrients, including Ca, Mg, and K as well as micronutrients, such as Fe, and nonessential elements, such as Si and Na (16). The authors contended that debates that question the potential of plants to weather rocks should consider weathering rates, as lichens (pioneer vegetation) show slower rates of weathering rock than higher plants, which have higher growth rates and an associated greater uptake of water and nutrients. Their experiments conveyed that most elements were released in the presence of plants (most for lupin and least for rape and maize). For instance, a 10-fold amount of Fe (a micronutrient) was released by maize at the end of 22 days (versus at the experiment's end of 36 days). Indeed, maize and banana had the highest uptake values. Ca and Mg peaked within plant tissue at 15-22 days, which was considered to be an early release, when biomass also peaked. Plant root-induced acidification of surfaces can lead to a significant dissolution of Ca carbonates. However, the dissolution (of basalt in this case) in the absence versus presence of plants did not conform to a linear or parabolic rate law. More in situ studies are needed to show the direct effects of higher plants on rock (and mineral) weathering. Nevertheless, these authors revealed a reduction in pH in the presence of plants (e.g. maize and banana, followed by lupin, but not rape), and this could be due to the production of CO_2 by root respiration as well as the release of H-ions by plant roots, which is controlled by plant growth.

The purpose of this study was to examine the causes for enlarged pits visible on an old wall at the University of Oxford Botanic Garden, UK (Fig:Ia). Their formation is predominantly due to chemical weathering due to dissolution in an acidic environment, including surface acidification from rootlets (as part of bioweathering) on varieties of ivy found on some of these border walls (Fig:Ib). Climatic conditions are also possibly involved in the formation of these pits, affecting physical weathering. Add: It is also important to consider the actual rock type and fabric, as this affects weathering rates and forms. Headington freestone is a buff-colored ashlar used on the border walls, spanning 100 m and up to 5 m in height, that was used in historical buildings in Oxford. This limestone is known to become encrusted with black crusts and is susceptible to blistering. Even though pits can also develop on this stone in acidic conditions, these holes are larger than usual pits visible on limestone walls from dissolution alone. It is possible that existing pits (formed due to acidification) were enlarged by physical weathering as a component of bioweathering (such as burrowing), as insects (such as bees) are known to inhabit holes on walls (Fig:Ic).

Fig Ia: Enlarged pits visible on the border wall at the University of Oxford Botanic Garden

Fig Ib: English ivy (*Hedera helix*) growing along the back (north-facing) wall

Fig Ic: Bee hotel located along the east-facing wall

2. METHODOLOGY: Pit dimensions were measured on 25 August 2012 using a 150-mm digital caliper with depth measure blade and 150-mm digital depth gauge calibrated through a zero function, both from BMI and with 0.01 mm resolution. Calibrated units were read in mm to two-decimal places. Acidity was measured using a digital pH meter directly in the field on 16 September 2013. This pocket-size pH 55 meter from Martini Instruments had automatic temperature compensation and a resolution of 0.1 pH, with readings to one-decimal place. The pH meter was calibrated regularly in the field using a two-point calibration (of pH 4.01 and 7.01). Finally, a digital lux meter (LX-1010B) was deployed in the field at a sampling time of 0.4 seconds and lux (lx) ranges up to 50000, with a resolution up to 100 lx (equal to 100 cd/m^2) and accuracy at 25˚C ±3˚C of ±5% + 2d. The instrument was calibrated to standard incandescent lamp at color temperature 2856 K.

The middle portion of the border wall was sampled at a height between 1-2 m. The orientation of walls was noted (at 306˚ for the west-facing wall; 35˚for the north-facing wall; and 132˚ for the east-facing wall). Sampling distance along the wall was 10 m on average and was restricted by border accessibility.

Measurements of pH were taken using runoff collection of squirted distilled water from the surface of blocks. This method employed APC Pure distilled water, with conductivity <0.02 ms; TDS <0.01 ppmn; BP 100˚C; and density of 1 gm/ml. The measured pH of the distilled water was consistently 6.8 and deviations from this indicated surface acidity/ alkalinity.

Finally, some preliminary (ad hoc) chemical analysis was performed on a couple of crusts and precipitate collected from the west- and north-facing walls. These materials were oven-dried and crushed using a mortar and pestle. ICP OES analysis was performed for % Al_2O_3, CaO, Fe_2O_3, K_2O, MgO, MnO, Na_2O, P_2O_5, SiO_2, TiO_2, SO_3, and volatile material (VM calculated at 950˚C) as well as Sr (ppm) separately for each of the three samples. Major elements were ascertained, as by (17), using an acid treatment of HNO_3 plus HF under pressure in a Milestone Ethos Sel microwave digester. Boric acid was employed to buffer diluted solutions, and determinations were made through the use of an Ultima 2 Jobin Yvon optical emission plasma spectrometer at the Chemical Analysis Laboratory, University of Salamanca, Spain.

3. RESULTS: There seems to be an overall trend of decreasing average maximum pit diameter along the span of border wall sampled in this study. The largest measured pit was 23.41 mm in diameter found at Site 3 some 30 m along the wall; the smallest was 3.32 mm across at Site 15 some 160 m along the border wall. Average maximum pit diameter appears for each site in Fig:IIa. These are greatest in the first 50 m along the west-facing wall and drop from then to comparable (lower) levels along the remainder of the wall (including similar north- and east-facing sections). Nearly half of the points are within 6 and 8 mm in maximum diameter, with anomalies at Sites 8, 10-11, 15, 18-19.

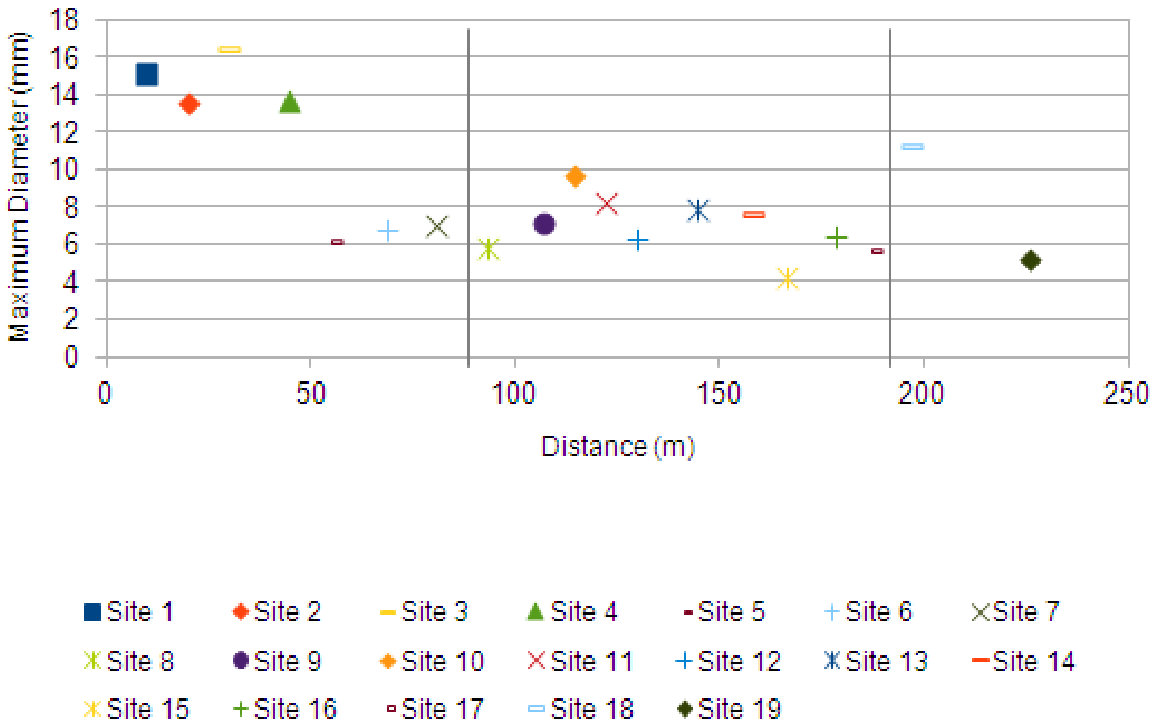

Fig IIa: Pit diameter measured along the sections of border wall (west-, north-, and east-facing, respectively)

Similarly, average pit depth seems to decrease along the wall, with sets of exceptions. Pit depth seems to decrease along the wall (Fig:IIb), with the maximum depth within the first 50 m (up to Site 4). The deepest pit was located on the east-facing wall at Site 19; it was 76.76 mm deep. The least deep of the pits appeared on the north-facing wall nearby at Site 17; it was 0.78 mm in depth. The general average depth was between 4 and 6 mm apparent from Site 6 to Site 17, with some anomalies at Sites 4-5, 9-10, and 18-19.

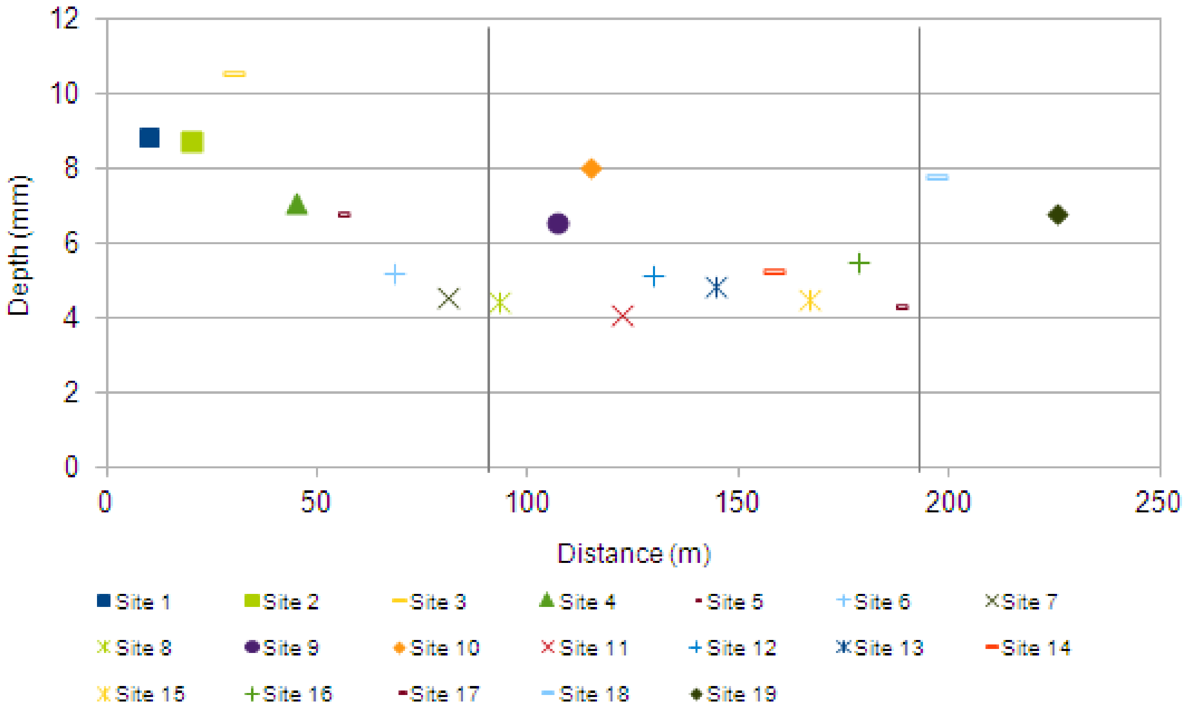

Fig IIb: Pit depth measured along the respective sections of wall

The number of pits counted per block seems to increase along the wall, with the lowest counts along the west-facing portion. These counts are generally between 40 and 60, with notable anomalies at Sites 11, 13, 16, and 19 (Fig:IIc). Unsurprisingly, pit density (pits/cm^2) tends to increase along the wall, most notably from Site 11 on the north-facing wall.

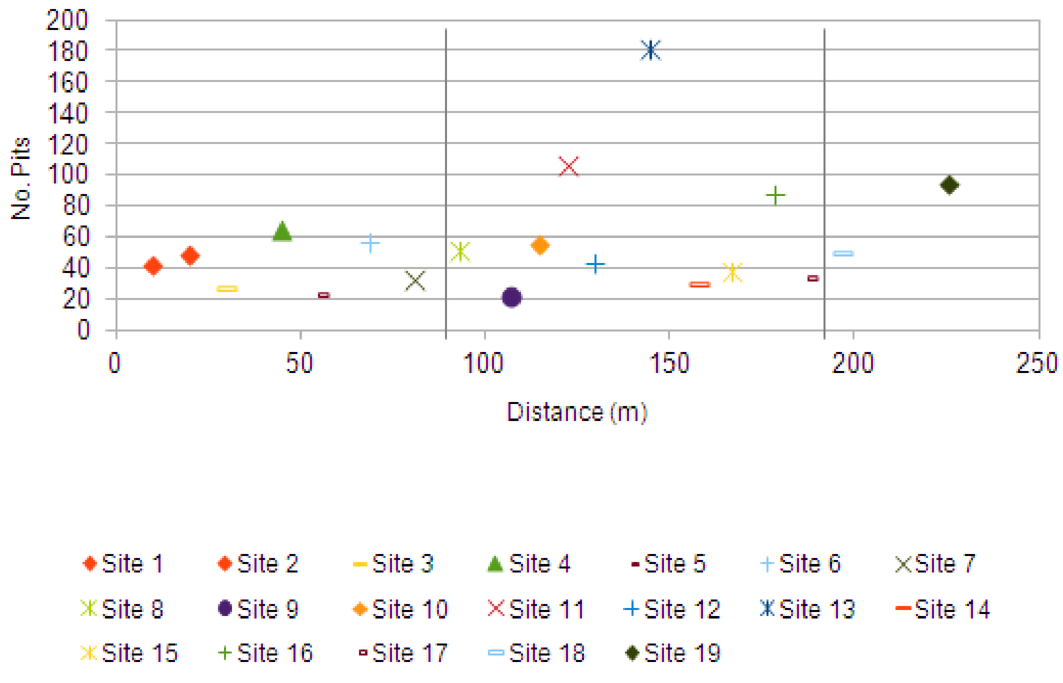

Fig IIc: The number of pits counted per block along these sections of the old wall

There was a general trend of increasing pH (reduced acidity) along the wall (Fig:IIIa), with r = 4611. However, this general relationship conceals orientational effects, such that pH increased along the west- and north-facing walls (r = 0.7262 and 0.8003, respectively), but decreased along the east-facing wall, where r = 0.9586 (Fig:IIIb).

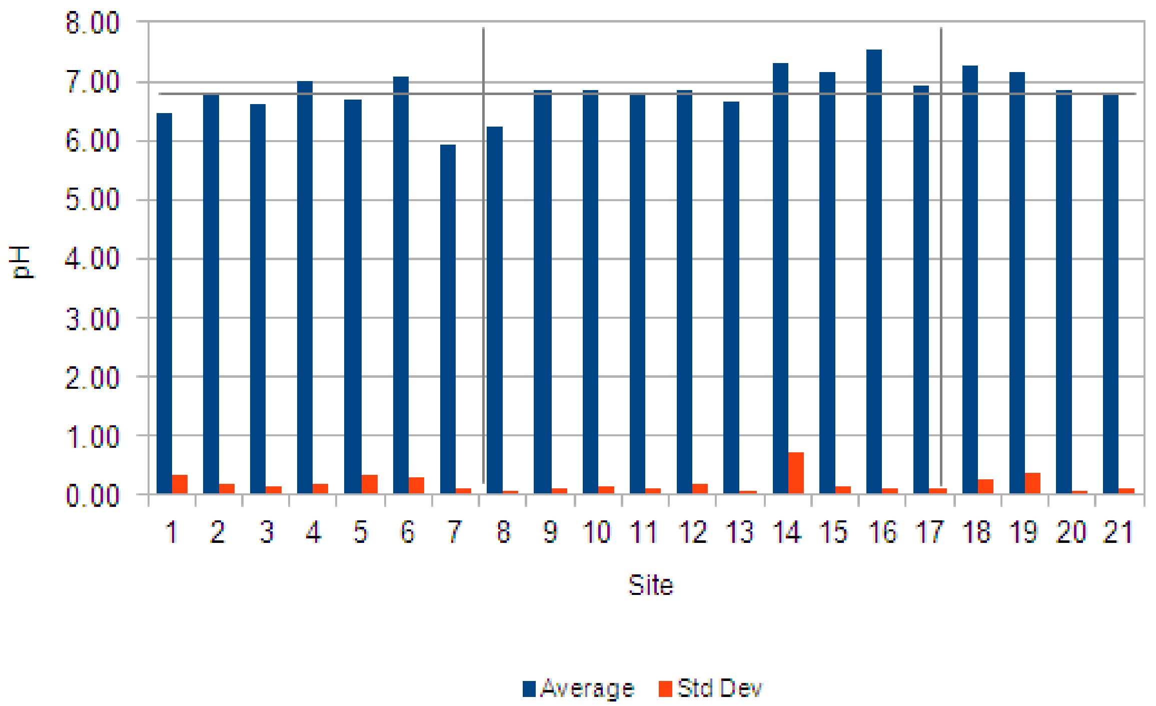

Fig IIIa: Acidity measured by pH along the west-, north-, and east-facing sections of the old border wall

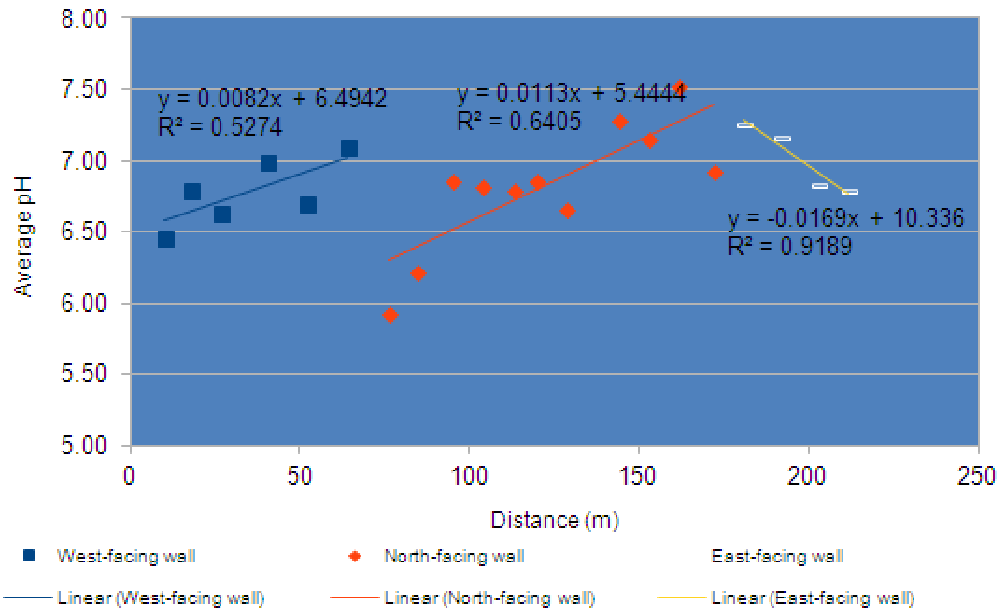

Fig IIIb: Linear correlation analysis of acidity along these sections of wall

Light levels were generally low between 51 and 15600 lx. They were greatest at Sites 6-8, where there was an archway that let in light from the south-facing exposure. The north-facing exposure and east-facing sections of wall had the lowest light levels.

In summary, the overall findings indicate the following general trends along the border wall from west- to north- and to east-facing sections:

- Decreasing maximum pit diameter and depth;
- Increasing number of pits and density;
- Increasing pH, except along the east-facing wall; and
- Lighting greatest at Sites 6-8 on the north-facing wall.

The ad hoc chemical analysis revealed similar results for the crusts, but variant results for the precipitate (Table:I). More specifically, the precipitate contained higher concentrations of most compounds tested, particularly Al_2O_3, Fe_2O_3,MgO, and SiO_2, with average differences of less than 1%. Concentrations of CaO and SO_3 were high across samples, especially in the crusts, where they were respectively 1.41% and 12.54% more concentrated on average than in precipitate. Sr was slightly more concentrated in the precipitate than in the crusts, with an average difference of 100 ppm. There was also notably more volatile matter (11.87% more) in the precipitate deposit than on average in the crusts.

Sample/ Element	**% Al_2O_3**	**% CaO**	**% Fe_2O_3**	**% K_2O**	**% MgO**	**% MnO**	**% Na_2O**	**% P_2O_5**	**% SiO_2**	**% TiO_2**	**% VM**	**% SO_3**	**Sr (ppm)**
Crust1	0.10	35.52	0.05	0.03	0.09	0.00	0.12	0.04	4.46	0.00	18.26	41.17	360
Crust2	0.11	34.13	0.25	0.05	0.08	0.00	0.12	0.02	4.46	0.00	19.02	41.92	320
Precipitate	0.27	33.42	0.46	0.11	0.32	0.01	0.13	0.08	5.07	0.02	30.51	29.01	440

Table I: Results of chemical analysis performed on two crusts and a precipitate deposit from the west- and north-facing walls (VM = volatile material)

4. DISCUSSION: Previous studies have indicated the work of plants on rock surfaces. Much work on biological weathering has been executed by Viles, for instance lichens weathering limestone at the Mendip Hills in Somerset, UK (18); blue-green algae on limestone at Aldabra Atoll, Indian Ocean (19); and some evidence that soiling increases with increased counts of fungi on limestone walls (20). Viles and Moses (21) observed that: "Many microorganisms are capable, through a range of etching and chelating processes, to bore and burrow their way into mineral surfaces producing distinctive boreholes, pits and channels" (p. 557). In polluted urban environments there are salt and biological interactions, such as with microorganisms found in gypsum crusts, whereby such organisms may adsorb salts and precipitate them. However, it is also possible that microorganisms may play a bioprotective role on stone, as by acting as a buffering layer that protects surfaces from salt action. For instance, biofilms were associated with case hardening in southern Jordon at Al-Quwayra, where microorganisms might have concentrated Mn, Al, Fe, and Mg on crusts (22). There were visible signs of biological weathering associated with a microfloral layer, including boreholes and etch pits (23). Nevertheless, the author also observed that calcified cryptoendolithic cyanobacteria contributed to surface consolidation and pore-filling.

More recent publications (academic and otherwise) by Viles have addressed the impact of ivy (*Hedera helix*) on old limestone walls. For instance, Sternberg and colleagues (24) recently made a case for *Hedera helix* L. acting as a particle sink; and also relayed its role as a climbing plant of reducing extremes in temperature and relative humidity on walls (25). Nevertheless, Carter and Viles (26) relayed that lichen color affected temperature (with a black coloration increasing the thermal gradient) beneath lichens like the epilithic lichen *Verrucaria nigrescens*. Work on the endolithic lichen *Verrucaria baldensis* has revealed both bioprotective roles as well as potential for biodeterioration. For instance, McIlroy de la Rosa and colleagues (27) examined the mesoscale formation of biotroughs following endolithic lichen colonization and biopitting due to fungal hypthae at the microscale at the Burren, County Clare, Ireland (see their Figure 5, p. 379). The type of lichen makes a difference on the impact that it has on stone. For this reason, it is important to further examine plants at the species level. For instance, the role that climbing plants (e.g., ivies) have on walls differ, with English ivy secreting acids and other climbers, such as Boston ivy, using suckers (a nonchemical means) to adhere to surfaces. Thornbush (28) conveyed that plant-covered surfaces have more potential for chemicobiological weathering (see her Figure 3, p. 236). It should also be noted that higher plants have more of a biodeteriorative capacity than lower plants, such as lichens.

Researchers have discovered that the pH around planted pots (of higher plants comprising fine roots) decreases by 1-1.5 units in comparison to blank pots in experimental trials (29). The plants released Si (rice), Ca (maize and soybean), Mg, and Mn (maize, soybean, and rice) in particular. Other elements, such as Fe and Al, were precipitated or adsorbed on surfaces as oxides and these appeared in low concentrations in the solutions of planted pots. The authors concluded that: “i) The proximity of the fine roots to the andesite particles caused a variation in the release of elements from the rock particles and ultimately in the uptake of elements by plants; ii) direct contact of fine roots on the rock particles could be one of the important processes to adsorb some of nutrients such as Si and Ca; and iii) weathering may be one of the consequences of the physiological activity of plants” (p. 65). The mechanism is chemical dissolution, which produces organic and inorganic acids through root exudes and root respiration, which enhance weathering. This is associated with the uptake of nutrients by higher plants for growth.

Measuring outdoor illumination is a relevant parameter in this research because of the impact of irradiation on microclimate and biological weathering, as through the growth of plants, affected by orientation. The light meter employed in this study was able to detect increased levels of illumination with exposure to the south face. This microclimatic effect has indirect effect on weathering through the appearance of light-sensitive organisms, such as photosynthesizing plants. Ivies are most affected by moisture-limited conditions, and sunlight would evaporate moisture (from the ground and walls), making it a drier environment for the plants to grow in. For this reason, these plants prefer to grow in the shade, where there are sufficient levels of moisture. This can be found on the north-facing wall in the study area as well as on the east-facing wall; however, this is where the bee hotels are located and this would affect the placement of climbing plants against these walls.

Fig IVa: Precipitates found along the back (north-facing) wall nearby to English ivy (*Hedera helix*)

Both the west- and north-facing walls are covered in climbing plants (ivies), including English ivy where precipitate is visible on the back (north-facing) wall. Using the chemical analysis (see Table:I) for guidance, it is possible to discern that crusts contain slightly higher proportions of CaO and SO_3 than precipitate, but that the precipitate has an abundance of most of the other compounds tested, including Fe_2O_3, K_2O, MgO, VM, and Sr. Higher concentrations of Ca is expected in crusts, but is also contained in precipitates, which comprise of Ca and Mg (hence, MgO). The sulfation process accounts for the high levels of SO_3 in crusts. The chemical signature is, therefore, not surprising. However, it is interesting that precipitates most noticeably occur in the vicinity of English ivy on the back wall (Fig:IVa). This could be attributed to the lower average pH evident in this section of the border wall. It is possible that English ivy in this section is secreting acids that are further acidifying the wall, resulting in the precipitation of Fe and Mg as well as Ca from its limestone fabric.

Where the enlarged pits are concerned, solitary (red mason) bees are likely culprits, as they are known to bore into soft material (e.g., mortar) to build their hives. These insects occupy pits (and enlarge them for their purposes) elsewhere in Oxford, as at Merton College (Fig:IVb). Other insects, such as spiders, are also known to occupy pits formed through dissolution in acidic environments such as this (e.g., spiders at the entrance of Worcester College, Oxford). However, it is noteworthy that the enlarged pits occurred throughout the surface of stone blocks (on hard stone, limestone in this case) and were not particularly located solely nearby mortar.

Fig IVb: Similar pitting observed on a different wall (belonging to Merton College, Oxford) known to be occupied by bees, with boring preference near to mortar

5. CONCLUSION: This study examines bioweathering through enlarged pits visible on an old border wall located in the University of Oxford Botanic Garden. Various analyzes conveyed the complexity of the problem, even within the auspice of bioweathering, since both plants (English ivy) and (solitary) bees may be responsible for the damage. A spatial analysis along the wall (from west-, to north-, to east-facing sections) revealed decreasing maximum pit diameter and depth; increasing number of pits and density; increasing pH (except along the east-facing section); and lighting greatest on part of the north-facing wall, where there is a passage through to the south-facing exposure. Chemical analysis showed typical patterns of greater proportions of Ca and S on crusts, with precipitated content having an abundance of Fe, K, and Mg as well as volatile material and Sr. These results support results from previous studies (e.g., since (1)) that demonstrate the impact of plants (plant roots, such as ivy rootlets, in particular) on rocks. These extracts were especially evident in the vicinity of English ivy, where it was locally more acidic, where precipitate was most noticeably found along the back wall. However, whereas acidity creates pits through the process of dissolution, insects (red mason bees, in this case) are responsible for enlarging the preexisting pits for occupation.

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