INTRODUCTION

The investigations incorporated in this thesis were initiated under the able guidance of Dr. D.K. Upreti, Assistant Director, Lichenology Laboratory, at National Botanical Research Institute, Lucknow. Since the research work was related with the lichen flora of some major historical monuments and buildings of Uttar Pradesh, the survey and collections of lichens were initiated from Lucknow district itself. Almost all the historical monuments and buildings of Lucknow were surveyed for collection of lichens. Apart from Lucknow some major monuments of Agra, Allahabad, Faizabad, Kanpur and Varanasi districts were also surveyed under the present study.

Sometimes it was not possible to collect lichen samples from the protected monuments. Therefore, the samples from a near by abandoned monument having similar construction material to the protected monuments were collected.

Most of the lichens growing on monuments and buildings are not prominent. They appear as black brown patches more distinct on the vertical surface of plaster. During rainy season, with increase of humidity their thalli assume the natural colour, swell and attain their normal dimensions. Thus they are more distinct in appearance during rainy season. For the rest of the year and also during long dry spells in the rainy season these plants seem to remain in a dormant condition.

In the course of biological succession on any bare substratum the vegetation that appears first comprises of bacteria, cyanobacteria, algae, fungi and lichens. The lichens being more conspicuous of all is easily recognized. These pioneer plant communities creates conditions that are conducive to the establishment and growth of other plant groups that are bryophytes, ferns and other higher plants. The vegetation
cover provides shelter to a variety of animal forms, like small arthropods, their larvae, nematodes, tiny earthworms and molluscs.

Lichens are hardy plants, they grow and thrive under conditions which other plants find unfavourable for their survival. Their slow rate of metabolism results in their sluggish growth. This phenomenon reduces their water and nutritional needs to the minimum, and as a consequence lichens are able to withstand xeric conditions for prolonged periods. They can also tolerate extreme range of temperature. Bare and exposed monuments and building surfaces therefore provide ideal, competition free situations for lichen invasion and establishment as pioneers of the bio-succession.

When lichen propagules invade the monuments and lodge themselves on their surfaces, they are too minute to retain any appreciable amount of moisture in their body for any appreciable period of time. When the propagules develop into thalli, their water holding capacity increases with the increase in their biomass and in the area of the substratum they cover. Water that is mother of the most of the damaging factors of monuments and buildings is progressively contained in greater quantities and is retained for longer periods by developing thalli along lichens-substrate interface, the seat of all activities. Gradually, more and more areas are covered by lichen growth.

Association of lichens and monuments are a common sight throughout the world. The effect of lichen growth on monuments has been variously interpreted. Many species of lichens have the ability to grow on bare rock. Nature has bestowed upon them the property of making use of conditions, which are unfavourable to any other life form. They are able to tide over prolonged desiccation and extreme temperature, coupled with a long life and slow growth-rate, that matches well with the slow release of nutrients from unweathered rocks. The other adaptability to cope with
such situation is their ability to stick, to penetrate in, and to digest rock material. Out of the three main kinds of lichens, the crustose forms are closely attached to the substratum by means of their medullary hyphae and are, in most cases not easily separable from the substrate.

Sometimes these lichens penetrate the substratum up to a depth of few millimeter and called as endolithic. The leafy, foliose forms of lichens are loosely attached to the substratum and their organs of attachment are hair-like structures called rhizinae or haptera. In absence of these hair-like organs the thallus is attached to the substratum by the lower cortex, the hyphae getting adglutinated to the rock surface. The foliose lichens can be detached more easily than the crustose ones. The thread-like or shrubby fruticose lichens are either erect or hanging, and are attached at a point can easily be pulled out.

The crustose lichens with close contact to their substratum are more effective agents of biogeochemical weathering than foliose and fruticose forms. Within crustose lichens the endolithic ones that grow inside the rock and are less conspicuous than their epilithic brethren perform job more efficiently as stone biodeteriorators than the latter.

In determination of the composition of the lichen flora on a particular monument, the climatic conditions play an important role. Type of lichen growth is a manifestation of interaction between ecological as well as geographical factors. Within broad macroclimates, several micro environmental conditions develop to many causes and the lichens in these niches show deviation in floral elements.

Environmental pollution plays important role in eliminating large number of lichen species in an area, as they cannot tolerate the acidic gases being very sensitive to them. Thus in areas with high acidic gases the lichens has no chance to invade
monuments. A few resistant species that perhaps, could not compete with other lichens in earlier unpolluted atmospheric condition find a competition free field to thrive, or even some species get metabolic stimulation by certain pollutants. They thus spread rapidly. Some of such lichens are highly virulent as stone biodeterioration agents. In Rome, which is a highly environmentally polluted city, a member of toxitolertant lichens species exhibit aggressive behaviour, spreading rapidly, covering a variety of substrate replacing the disappearing harmless or less harmful species that are susceptible to air pollution. Under these conditions it is necessary to determine the interaction between species of lichens and monument stone surface. Such an increased lichen activity, coupled with direct action of pollution clearly explains, why the monuments apparently unchanged for centuries in the past appear now vulnerable to deterioration by lichen attack. Such a situation has arisen because of two reasons, the first one is that certain lichens have been able to exploit changed environmental conditions and/or the another is monuments were deliberately protected from lichen attack in the past.

Collection and documentation of lichens of monuments and building is an important aspect from floristic angle. A large number of floristic studies regarding Indian lichens are available. However, owing to the large extend of the country only few reports on lichens of Indian monuments are published. The lichens in few monuments of Karnataka, Orissa and Uttar Pradesh are studied so far from India. The studies of lichens on monuments are limited to the Lucknow City only in the Uttar Pradesh. Owing to the vast and diverse cultural heritage in the past, the state of Uttar Pradesh have a wide variety of historical monuments and buildings. Some of the historical buildings in the region are looked after by the government agencies like Archaeological Survey of India (ASI), but a large number of the monuments are
uncared and bear a luxuriant growth of lichens together with other plants growth.

Thus, to get an information on the lichen taxa growing on different monuments and buildings of Uttar Pradesh, the present study is initiated with the following objectives-

1- Survey, collection and identification of lichens from different monuments and buildings of Uttar Pradesh.

2- Inventorization of lichens growing on various monuments of Uttar Pradesh.

3- To conduct the ecological studies on the lichen flora of different monument.

4- To provide detail account of the control measures and recommendation for conservation of the monuments of Uttar Pradesh.
LICHEN ACTIVITY ON MONUMENTS AND HISTORICAL BUILDINGS

World scenario

Rocks have been symbolized for qualities like, strength, firmness, solidity and confidence. “Rocks are as eternal and solid as time” (Polzer, 1982). One finds huge rock faces on mountain slopes and large boulders elsewhere unchanged, unaltered since time immemorial. It is because the break down of minerals, in general, is an extremely slow process (Brodo, 1973). The tenacity of rocks defies the action of diverse rock-weathering agents and provides them resistance to rapid disintegration. For this quality, as well as inexpensive and easy availability, man has put stone material in use for various purposes. Prior to discovery of metals, stone was the principal material for making tools and other objects. This period called “Stone Age”, enjoyed fairly long span of time in prehistoric era of the story of mankind. Many of the stone objects dating back to our glorious past and hopefully, will continue to do so for centuries to come. As Polzer (1982) has written, “it brings the past to the present in monumental, tangible and vivid form”. In contrast, most of the ancient objects made of other materials (including metals, with harder consistency, but showing greater proneness to chemical transformation) have in course of time, been consigned to the junk yard of oblivion.

Yet, all that exists in this world today, is bound to meet its doom sooner or later. Stone is no exception to this rule. Constant endeavour of a host of stone-weathering agents work singly or jointly to this end. Weathering of rock has been
defined as "the total effect of all processes involved in the disintegration (physical process) and decomposition (chemical process) of rocks" (Syers and Iskandar, 1973).

Climate is the mother of almost all the rock weathering factors. Durability of stone depends on its resistance to a wide range of factors, such as freeze-thaw cycle, wetting and drying cycle, wind-blown dust, infra red heat, and ultraviolet exposure (Scali and Stockbridge, 1982). Water is the prime agent responsible for all sorts of damages to rocks. Deterioration of stones is closely related to movement of fluids (water) through their interior, which are conditioned by the frequency of pores, their size and degree of connection between them (Ordazand and Esbert, 1985). Entry of water in rock through pores, capillaries or by biological growth on or near rock surface, its retention period in the rock, its alternate freezing and thawing in its pores capillaries, cracks and crevices and presence of a variety of chemicals, including atmospheric carbon dioxide and biogenically produced organic acids in solution make water immensely important in rock weathering process. Role of water gains further significance in tropical climate where moist conditions prevail almost all the year round. Lot of attention has been paid by several workers (Hale, 1975; Riederer, 1981; 1984) about rapid deterioration of archaeological stone monuments in Sri Lanka as well as Guatemala and Honduras respectively.

Climate, of late, has acquired sharper teeth for rock weathering phenomenon by incorporating an additional, man created factor, called environmental pollution. Many air pollutants are acidic in nature and react with the rock material at its surface. Despite his views quoted earlier, Polzer (1982) agrees that stone is vulnerable to many factors, including pollution that cause decay of stone. Smoke and gas pollutants of the air contain particulate material consisting of soot and tar-like substances as well as sulphur dioxide vapours, nitric oxide, aldehyde, sulphates and chlorides (Strzelczyk,
1981). The climate play indirect role that manifests itself in the form of diverse type of biological growth on rock surface. These biological forms contribute to rock disintegration by their metabolic activity. The type of biological growth depends on the nature of stone, climatic conditions and degree of air pollution (Richardson, 1976).

The biological elements responsible for altering stone material are many; bacteria, fungi, algae, lichens, that cover the rock, capturing the dirt and in the long run transforming themselves into agents of corrosion (Jaton et al., 1985). In addition to these plant groups, other organisms that inhabit the rock surface are actinomycetes, cyanobacteria, bryophytes, higher plants, and large number of animal forms, namely mites, spiders and larvae of many insects. The stones that are exposed to the atmosphere develop microbial mats, i.e., biofilms (Krumbein, 1987). They change the mineralogical and chemical composition of the original rock surface. Stability, permeability, colour and density of stone are affected. This mat may cause crust formation inside or outside rock mineral. Iron and manganese are translocated by the microflora from deeper parts of rock to or near its surface. They are oxidized and cause colour change of the rock surface. Deeper layers thus devoid of these elements become weak, resulting in exfoliation of rock from the weakend part. The effect of algae, lichens, trees and animals on rock corrosion has been investigated in relation to interactions between their biofilm (Kotlik, 1983). The interaction of other cryptogams with lichens in rock biodeterioration process has also been investigated (Savoye and Lallemant, 1980). Colonization of calcareous rocks begins with green plants (algae and lichens), which gradually cause deposition of organic matter (Jaton et al., 1985). It leads to commencement of bacterial and fungal growth, that in turn also secrete organic acids and supplement to the rock weathering action of green plants.
Environmental pollution alters the ecology of a place and affects the composition of microbial film (Krumbein, 1988). Microorganisms show changed floral composition. Sometimes many harmless taxa are replaced by those showing aggressive behaviour towards rocks, and certain tox intolerant species may play havoc to the stone surface.

In the complex phenomenon of rock weathering under natural conditions any quantitative assessment of the harm caused by individual factors separately is not possible. “In nature biodeterioration of stones cannot be considered as an isolated phenomenon, in fact it always occurs with other physical, chemical or physio-chemical deterioration process with which it is strictly correlated. The interaction of these various weathering agents must always be considered” (Caneva and Salvadori, 1988). In the laboratory, however, the influence of a single organism on any one mineral or a variety of minerals can easily be investigated (Jones et al., 1980).

Out of the total array of abiotic as well as biotic rock weathering factors, the subject matter chosen for this study narrows down our consideration to a single group of plants, the lichens. Studies undertaken in respect to them so far, mainly speak of the qualitative aspect of the damage done. Although a good deal of work has been carried out on this topic, views differ about importance of lichens as rock weathering agents. Some consider them as effective biodeteriorants of rocks by their physical and chemical activities, whereas other think that such a role attributed to this group of plants has been over emphasized. Much knowledge is yet to be revealed on the interaction between lichens and minerals (Jones and Wilson, 1985).

Many species of lichens have the ability to grow on bare rocks. Nature has bestowed upon them the property of making use of conditions which are unfavourable
to many other life-form. They are able to tide over prolonged desiccation and extreme temperatures, coupled with a long life and slow growth rate, that matches well with the slow release of nutrients from unweathered rocks. The other adaptability to cope with such situation is their ability to stick to, to penetrate in, and to digest rock material (Topham, 1977). Broadly speaking, there are three kinds of lichens according to habit, they are, crustose, foliose and fruticose. Crustose forms are closely attached to the substratum by means of their medullary hyphae and are, in most cases, not easily separable from it. Sometimes these lichens penetrate the substratum (rock) and become endolithic. Foliose forms are loosely attached to substratum and their organs of attachment are rhizinae or haptera. In absence of these organs in some species, the thallus is attached at places by its lower cortex the hyphae getting agglutinated to rock surface. Foliose can be detached more easily than the crustose ones. Fruticose forms are either erect or hanging, and are attached at a point and can easily be pulled out.

Crustose lichens with close contact to their substratum are more effective agents of biogeochemical weathering then foliose and fruticose forms (Krumbein, 1988a; Krumbein et al., 1987). In the crustose forms the endolithic ones that grow inside the rock and hence less conspicuous than their epilithic brethren perform job more efficiently as stone biodeteriorants than the latter (Danin et al., 1982; Krumbein, 1966, 1969).

In determining the composition of the lichen flora, again, climatic conditions play an important role. Type of lichen growth is a manifestation of interaction between it and ecological as well as geographical factors (Krumbein, 1988; Krumbein et al., 1987). Within broad macroclimates, several micro-environmental conditions develop due to many causes and the lichens in these niches show deviation in floral elements (Seaward, 1979).
Attention of conservationists of cultural property was attracted by acceleration of deterioration rate of stone art work during a few preceding decades. This phenomenon was more pronounced in industrialized urban areas where the air was rich in acidic chemicals. Environmental pollution plays significant role in eliminating large number of lichen species, as they cannot tolerate soot and sulphate and thus have no chance to invade monuments in such areas. A few resistant species that perhaps, could not compete with other lichens in earlier unpolluted atmospheric conditions find a competition-free field to thrive, or even some species get metabolic stimulation by certain pollutants. They thus spread rapidly. Some of such lichens are highly virulent as stone biodeteriorating agents. In Rome (an environmentally polluted city) a number of toxitolertant lichen species exhibiting aggressive behaviour, spreading rapidly, covering a variety of substrate replacing the disappearing harmless or less harmful species that are susceptible to air pollution have been reported (Seaward and Giacobini, 1991). Under these conditions it become necessary to determine the interaction between species of lichens and monument stone surface. Such an increased lichen activity, coupled with direct action of pollutants clearly explains why the monuments apparently unchanged for centuries in the past appear now vulnerable to deterioration by lichen attack (Seaward, 1988). Such a situation (Jenkins and Middelton, 1988) has arisen because of two reasons; the first one is that certain lichens have been able to exploit changed environmental conditions, and/or the another is monuments were deliberately protected from lichen attack in the past.

Weathering of natural rocks is beneficial phenomenon from human point of view as it leads to the formation of soil, but when the same process overtakes the rock material used in man-made objects it becomes a matter of concern. In these stone objects, it is the surface that determines the artistic expression of sculptures, portals,
monuments, and many other elements of architecture, that is directly affected by weathering action. It leads to irreparable loss to our cultural heritage (Eleonora and Heuck-Vander Plas, 1968).

Physical and chemical properties of the substratum also have a hand in determining the type of lichen growth on it. The most important of which are texture, water relations and chemistry (Brodo, 1973). Rough surface provides better lodging place to lichen propagules than smooth surface; softer parts of rocks consisting of mica, offer more favourable niches for lichen establishment, at least initially. Concerning water relations, different rock types absorb, retain and release water at different rates and to different degrees. Water relations over the rock surface change with establishment, colonization and spread of lichens on it. These factors play an important part in biodeterioration of rocks. The lichen propagule (soredium) on invading and setting on rock is hardly able to retain any moisture in it and its moisture content is thus, nearly the same as that of the substratum surface (Scott, 1967). With the development of propagule into a thallus, however, the time lag between the saturation-evaporation cycle of the thallus and the substratum gradually increases. With further increase in the thallus area there is progressive decrease in the evaporation rate from the rock surface. When the whole rock surface is covered by the lichen growth the foliose forms start overlapping each other, affecting further change in wet-dry ratio because of greater water retaining ability of the lichen cover. This phenomenon provides a good example of biologically induced change in the water content of the rock surface. The thallus of crustose lichens too, have a good moisture retaining ability. It delays removal of water from rock surface by capillary retention, particularly in case of cracked areolate thalli, the spaces between areoli being sufficiently small to hold water against gravity flow.
In consideration to chemistry of substratum, three factors need attention are, minerals, pH and organic nutrition (Brodo, 1973).

Lichen communities of different substrata in British Isles have been extensively surveyed (James et al., 1977). On hard limestone (e.g. Carboniferous and Devonian) several distinct lichen communities were observed, most of which also grow on soft calcareous rocks. On a calcareous tombstone at Cobham churchyard, Surrey, Buellia canescens, Caloplaca aurantia, C. saxicola, Lecanora dispersa, Physcia ascendens, P. orbicularis and Xanthoria aureola have been reported as predominant species. On other basic sandstones, two specialized communities were noticed. On the other hand siliceous rocks support more lichen species forming many communities. James et al. (1977) also lay emphasis on certain factors that control development of this community.

The organic material acquired by the rock is important in determining lichen as well as the other microorganism growing on its surface. Organic matter, apart from atmospheric dust comes from soil. By capillary action of the porous rock material soluble organic nutrients reach great heights of the monuments. Urban soil is fertilized by sewage, animal excrements, and organic remains. Pigeons commonly abound old monuments and their excrement acts as a fertile medium for biological growth. In addition to its direct damage to rocks by secretion of acidic products, it promotes growth of nitrophilic microorganisms, including lichens, certain species of which may be active in substrate corrosion (Bassi and Chiatante, 1976). Some rocks, by themselves are rich in organic substances, because of the way they are evolved (Strzelczyk, 1981).

Rock weathering action of lichens is a well known phenomenon (Lindsay, 1965) and is known since ages. In a cleavage of schist, due to Verrucaria marmorea
and *Baeomyces rufus* (Topham, 1977), the mycobiont hyphae were found penetrating rock to the depths of 1.9 cm and 1.0 cm respectively. There are other reports of deep penetration of lichen hypha into stones (Richardson, 1976; Syers, 1964).


Summarizing earlier data on the effect and significance of lichens, particularly the crustose saxicolous forms, on rock (natural or building and monumental stones, Jones *et al.* (1987) documented weathering of rocks, formation of secondary products, and effect of lichen acids.

**Process of rock deterioration by Lichens**

Three kinds of damages are known to rock material by its interaction with microorganisms that are mechanical, chemical, and soiling (Hueck, 1965). Lichens degrade stone in the following ways:

(a) through increase of their biomass as they grow;

(b) through changes in volume of wet and dry periods resulting in repeated relaxation and shrinking of colony – this is particularly important for organisms with a strong adhesion to the surface;

(c) through their water binding capacity, by which they can exert considerable force in winter frosts;

(d) through excretion of organic acids;
Rock-weathering process by lichens through biogeophysical and biogeochemical disintegration of minerals is reported (Syers and Iskander, 1973). The former process is brought about through rhizinal-penetration, haptera detachment and expansion and contraction of thallus, and the latter through biogenic production of carbon dioxide, oxalic acid and lichen acids. The lichen acids damage rocks by chelation or complexing action. Hueck (1965) and Syers and Iskander (1973) presented the detail account of weathering by lichens.

Physical Process

By organs of attachment and expansion and contraction of thallus

Most of the foliose lichen thalli possess rhizinae on their lower surface, which act as organs of attachment to the substratum (Fig. 1,4). In some other lichens, such as, Collema and Xanthoria, the same role is performed by haptera. There structures are thicker than rhizinae and their distal ends consist of tufts of loose hyphae that attach haptera to the rock. Some of the foliose and most of the squamulose lichens lack these structures, and such cases the lower cortex of the thallus takes over the function of attachment (Fig. 2). In crustose forms the loosely arranged medullary hyphae running periclinally in relation to the substratum are directly attached to it (Fig. 3). All the organs attached to the substrate surface by gelation or mucous produced by lichen, which causes physical corrosion of rocks (Gehrmann et al., 1988). In dry condition it produces high adhesive strength between structural components of stone (Eichler, 1986; Fry, 1922, 1927). Furthermore, these substances themselves, are aggressive and active on rock surface. None of these organs of attachment are hard and strong enough as to be able to penetrate the hard substratum physically unless rock dissolving chemicals come to their assistance. They, however,
Fig. 1. Foliose lichen with rhizinal growth on lower side

Fig. 2. Peltate lichen with haptera on the lower side

Fig. 3. V.S. crustose lichen thallus without rhizinae

Fig. 4. V.S. lichen thallus with rhizinae on the lower side
do enter the rock along cracks and crevices on its surface. A wet thallus (Fig. 5) when starts drying up gradually, shrinks due to loss of water. The upper cortex of the thallus exhibits stronger response to drying process resulting in greater degree of shrinkage as compared to other layers of thallus (Fig. 6). Such phenomenon tends the thallus to curl up, exerting a pulling strain on the organs of attachment. Initially this force is resisted by these organs, but as the strain increases, on further drying of thallus, the former either break or are lifted along the thaline margin, detaching minute particles of the substratum because of strong adhesion between rhizinae and the substratum. On return of wet conditions the thallus regains its original shape and size and the organs of attachment fix themselves to the rock once more. This process goes on ad infinitum. In crustose lichens, the loosened substratum particles are incorporated in the thallus (Fig. 7).

The disintegration of superficial layers of rock substratum due to expansion and contraction of epilithic crustose lichens was more pronounced either at hypothallus around thallus margin or below apothecia (Fry, 1927).

Physical weathering process is affected to a far greater degree in the latter than in the former. Mycobiont hyphae are more or less gelatinous and are also embedded in thin mucilaginous film, both substances having great adhesive property. On drying of thallus these hyphae are pulled free of the substratum, dislodging and carrying with them rock particles (Fig. 6). At the centre of thallus where apothecia start developing the thalline arch upward, lifting superficial layers or particles of the substratum along with them. Formation of successive arches has been observed one above other as seen in the vertical section of the apothecia of Lecidea confluenus by continuous arching of hyphae during apothecial development (Fry, 1922, 1927). The rock material in these arches did not seem to differ chemically from rest of the substratum,
Fig. 5. Wet lichen thallus – flat on the substratum

Fig. 6. Dry lichen thallus – curled upward

Fig. 7. V.S. Lichen thallus with deposition of calcium oxalate crystals (A=hymenium; C=Cortex; Cr=Calcium oxalate crystals; P=Photobiont layer; M=Medulla)
denoting thereby mechanical action of lichens. Same condition was noticed in the apothecia of *Lecidea plana*, *Lecanora atra* (= *Tephrromela atra*) and *L. sulphurea*. Although arching of hyphae is always there at apothecial sites, in harder rocks, such as harder shales, schist, gneiss, obsidian, Carboniferous limestone, no arching of substratum layers was observed but in all cases mineral particles in greater or lesser degree were shown to be embedded in base of the apothecial tissue. In order to prove the mechanical action of gelatinous hyphae, experiments were carried out by fixing gelatinous replicas of apothecia to rock substratum (Fry, 1927). Successive drying and wetting of the replicas resulted in more or less similar observations as that in case of lichen apothecia.

Porous sedimentary rocks of calcareous nature are particularly susceptible to physical penetration by lichens (Lloyd, 1973). The presence of disintegrated rock surface below saxicolous lichen thalli has been reported and considered that physical disintegration provides increased rock surface for chemical weathering process (Syers and Iskandar, 1973). Nonetheless, chipping of minute rock fragments is undoubtedly the result of biogeophysical weathering of rocks. Enjoying greater freedom of movement due to nature of their attachment to rocks, foliose lichens are probable more efficient biogeophysical weathering agents. Loosening of minerals in form of granules is caused by chemical weathering but their detachment from the parent body is by physical activity of lichens (Jones and Wilson, 1985).

The phenomenon of biogeophysical weathering caused by lichen activity has also been observed in archaeological materials.

Limestone and bricks at Giralda of Seville, Central Italy, apart from chemical weathering by crustose lichens, were also being damaged physically (Saiz-Jamenez, 1981). It was demonstrated by removing part of thallus of crustose lichens
mechanically, with which a 1-2 mm thick substratum layer was also detached. This has also been observed on monuments at Lucknow, India (Singh and Upreti, 1991). On brickwork of a historical monument in Sri Lanka, detachment of a thin layer of substratum by rolling up of dry lichen thalli, causing considerable damage has been expected (Riederer, 1981, 1984).

While determining the relative importance of species of lichens in biodeterioration of wide range of archaeological materials in Central Italy. Many lichens create microclimate at thallus-substrate interface particularly in terms of water relations that lead to mechanical damage to stone-work in ten years of less time (Seaward et al., 1989).

**Water binding capacity of thallus**

This process is relevant to cold places where moisture contained in lichen thallus, particularly in endolithic parts expands after freezing during cold spells, exerting great pressure on surrounding stone material causing the existing cracks and crevices to widen, dislodging rock fragments. There seems no record of monument-stone deterioration by the process.

**Chemical process**

Biogenically produced carbon dioxide by lichens is one of the major rock weathering agents though, insignificant (Syers and Iskandar, 1973). But according to Jones and Wilson (1985) some lichens in tropical climate, where organic acid anions are drained, and by a hydrolythic process minerals of rocks are disintegrated through depletion of basic cations (K⁺, Na⁺, Mg²⁺, Ca²⁺) and silica, that ends up in accumulation of Al and Fe.
Carbon dioxide is universally present and when dissolved in water makes an acidic solution which reacts with a variety of rocks. Considering total mass of lichens in comparison to other green plants, coupled with their innate quality of slow metabolic activity so essential for their survival in the conditions they live, their contribution to carbon dioxide production under whatever climatic conditions seems to be to a negligible percentage of the whole.

Various studies pertaining to the ability of lichens for disintegrating their mineral substrate by chemical means appears mainly related to the excretion of some organic acids and lichen substances by the mycobiont hyphae. Crustose lichens were described by Linnaceus (Smith, 1962), as “the first foundation of vegetation” and Plitt (1927) stated about them as “though hitherto we have considered theirs a trifling place among plants, nevertheless they are of great importance at that first stage in the economy of nature”. These very plants play the dominant role in chemical breakdown of rock minerals. Process of rock weathering by them is discernible at rock-lichen interface below crustose lichen thalli. The effect of excretory products of lichens on the mineral surface makes it appear as honeycombed with etch pits, trenches as well as other features of chemical alteration due to clearly visible extensive corrosion, as the minerals lose their integrity (Jones et al., 1981; Wilson and Jones, 1983). Sometimes the inter-grain cementing substances are acted upon, resulting in loosening rock mineral grains (Jones and Wilson, 1985). More pronounced chemical weathering of basaltic lava flow in Hawaii below lichen thalli than in lichen-free areas has been observed (Jackson and Keller, 1970a, 1970b).

Earlier work was mostly on physical action of some lichens, e.g. *Lecidea confluens*, *L. plana*, *Lecanora soredida*, *L. atra* (*Tephrumela atra*) *L. sulphurea*, *L.*
parella, Rhizocarpon geographicum, Aspicilia alpina and A. calcarea on different types of rocks (mentioned earlier) and did not touch upon the chemical aspects (Fry, 1922, 1927). Change of colour and texture of schist fragments below apothecia of Lecanora sordida and obsidian mineral modification beneath those of Aspicilia alpina and Rhizocarpon geographicum are due to chemical reactions (Fry, 1927; Jones and Wilson, 1985). Pitting of rock surface observed after removal of lichen cover also bears testimony to the same. Chemical weathering of rock below lichen thalli during their occasional wetting in the desert atmosphere of dry south-western part of North American continent has been reported (Weber, 1977).

In recent years increasing use of modern and sophisticated analytical techniques, such as, atomic absorption spectroscopy, electron probe microanalysis, scanning electron microscope (SEM), transmission electron microscopy (TEM), X-ray diffraction analysis (XRD), Raman microscopic analysis, X-ray energy dispersive analysis (EDX), and laser scan microscopy (LSM) have paved way for correctly portraying the rock-lichen interface and identifying the products of rock disintegration by the action of biogenic organic acids.

The scanning electron microscopy and other light microscopy methods are useful for analysis of the studies related with effects of microflora on rock substrata the degree of hyphal encroachment into rock sample can be documented photographically.

The polarized microscopy helps to know the size and orientation of the rock grains. The distribution of particles can be examined by the polarized microscopy in rocks, which are very hard and most of the difficult to cut.
The X-ray diffraction (XRD) analyses helps in order to establish the mineralogical composition of the sandstone samples. The whole XRD images can also be taken without reducing the sample into powder.

The environmental scanning electron microscopy (ESEM) imaging is a very powerful tool, especially when live organisms are present. In this device the vacuum in the chamber is much reduced thus there is no need to dry the organic tissue. Thus an interesting series of pictures that were assembled together in order are obtained, at high resolution, a complete cross section of the sandstone, from the surface to the bulk is available. These observation allowed us to establish the sandstone-lichen relationship and possibly the modification, if any, of the rock caused by the lichens.

SEM – BSE (scanning electron microscopy with back scattered electron imaging) involves two main steps. The first corresponds to the sample preparation procedure and combines glutaraldehyde fixing with post fixing in osmium tetroxide and preparing polisher resin blocks that are finally coated with carbon (Wierzchos and Ascaso, 1994). The second step involves the observation of the polished carbon-coated surfaces in the scanning electron microscope using the back-scattered electron (BSE) detector. The BSE signals is strongly dependent on the mean atomic number of the object bombarded with electrons. Thus, the SEM-BSE allows the ultra structural elements of the biological components to be identified, along with the simultaneous observation of the microhabitat's inorganic components, among which are the minerals that surround the micro-organisms (Ascaso and Wierzchos, 1994, 1995; Sanders et al., 1994; Ascaso et al., 1995).

Energy dispersive spectroscopy (EDS), a microanalytical technique, allows these mineral components to be characterized (qualitative/quantitative determination and spatial distribution of elements) (Wierzchos and Ascaso, 1996, 1998).
Formation of secondary products

Mycobiont hyphae of many lichens produce organic acids, mostly oxalic acid as their excretory product to whose action limestone is very prone. Calcium carbonate of the rock is slightly soluble in water and is acted upon by oxalic acid. By such action many lichens sink into the rock material and become endolithic (Syers and Iskandar, 1973). Action of oxalic acid on metallic ions in the minerals produces insoluble substances, e.g. oxalates, that are deposited within the lichen thallus as extra cellular compounds (Jones et al., 1980; Wilson et al., 1981). Braconnot (1825) was perhaps the first to notice calcium oxalate crystals in lichen thallus. According to Syers and Iskandar (1973) the biogenic production of oxalic acid does not pose a serious threat to rocks. By means of thermal techniques the calcium oxalate contents of many lichens have been estimated and it has been suggested that accumulation of appreciable amount of this compound may be the characteristic of calcicolous lichens and not of all the species growing on the calcareous substratum (Syers et al., 1967). While investigating weathering of basalt masses of plate like calcium rich crystals were found associated with the hyphae of Pertusaria corallina colonizing this rock (Jones et al., 1980). These crystals were identified as whewellite, the monohydrate form of calcium oxalate. The same crystal has also been found occurring at the rock-lichen interface of limestone (Ascaso et al., 1982). The latter workers, in addition, found crystals of dehydrate calcium oxalate, weddellite, at the limestone and dolomite-lichen interfaces of Caloplaca collopisma and Diploschistes ocellatus.

Pitting of minerals and rocks is caused by lichen action (Krumbein and Krumbein, 1987). By means of photograph, Syers and Iskandar (1973) studied the interesting example of pit formation on rock surface caused by immersion of flask-shaped perithecia of an endolithic lichen Verrucaria sphinctrina. Such a penetration
in rock may be due to action of dissolved carbon dioxide in water (Fry, 1922) or by lichen compounds (Smith, 1921). Most probable cause of rock dissolution, however, seems to be by oxalic acid action. Similar pits were observed on exposed limestone face to the fructifications of another species of the same genus, that is, *V. rupestris* (Sollas, 1980). Other lichen species forming pits on rocks are *Caloplaca lactela*, *Ionaspis cyrtapsis*, *Lecanora calcarea*, *L. flavida* f. *caerulans*, *Opegrapha saxicola*, *Polyblastia intercedens* f. *abstrahends*, *Thelidium pyrenophorum*, *Verrucaria calciseda*, *V. hochstetteri* and *V. mamorea* (Pia J. Von, 1937), and *Protoblastenia rupestris* var. *incrustans*, *Sarcogyne pruinosa* and *Verrucaria calciseda* (Degelius, 1962; Eleonora and Heuck-Vander Plas, 1968).

**Analytical and experimental evidences**

By means of energy-dispersive X-ray analysis (EDX) the amount of calcium in deteriorated stones and the plants, including lichens has been determined (Bech-Anderson, 1984). It was observed that calcium was lost from the substratum and was gained by plants, denoting thereby, biological erosion of stones. Further, it was noticed that the growth of a lichen, *Umbilicaria* on plagioclase rock in Sweden was found to contain aluminium, silicate and potassium and at places calcium and iron oxide (Bech-Anderson, 1984). The lichen growth was generally restricted to calcium rich area and the thallus was found to accumulate high amounts of calcium and iron. In a species of *Xanthoria* in Denmark growing on amphibolite, the mycobiont hyphae penetrated in places rich in plagioclase (calcium containing mineral) but avoided calcium free amphibole mineral.
The effect of two biogenically produced acids, i.e., oxalic acid and malic acid on marble, coral sandstone and khondalite in laboratory resulted in dissolution of the calcium content of these rocks (Jain et al., 1991).

**Monument deterioration**

There are several examples of monument stone weathering leading to oxalate formation, an action that is attributed to lichens.

White encrustations on a marble column of the porch of the Church of Santa Fosca on the island of Torcello, Venice was found to be associated with thalli of *Caloplaca aquantia* and *Physcia* species, probably *P. caesia* (Lloyd, 1973). On the same island, similar effects were observed on marble columns of the porch of the Basilica of Santa Maria Assunta (Monte and Sabbioni, 1983; Salvadore and Zitelli, 1981). The weight accumulation of oxalate in lichen thallus was estimated to be around 50% of the total weight.

Lichens, particularly the crustose ones, are quite active in rock weathering at the world famous Borabudur Temple, Central Java (Siswowiyanto, 1981). XRD analysis revealed the presence of calcium oxalate in their thallus.

Changes have been observed on the surface of marble and limestone due to lichens on the front of Reggio Emilia in the valley of river Po, Italy (Monte and Sabbioni, 1986). Although air pollution was the major factor in bringing about weathering of these stones, a part of it was also attributed to algae and lichens, as calcium oxalate, both as weddellite and whewellite was found associated with them.

Biocorrosion and biopitting due to lichens results in crater shaped biocorrosion very frequently in Roman and Greek marble monuments (Krumbein, 1987). The pitting is clearly associated with epilithic and endolithic lichens of various species. On
a marble monument, Trajan’s Column at Rome, Italy, two changes were observed on
the surface, i.e., the brown patina, called scialbatura, and numerous holes, called pits
(Monte, 1991). According to Monte (1991) they were caused by oxalic acid secreted
by lichens, growing earlier over this substratum, but not due to highly polluted
atmospheric conditions prevailing over there. XRD analysis and SEM photographs
confirm this hypothesis by revealing presence of oxalate crystals and lichen fragments
respectively associated with these features.

In a patch of the crustose lichen, *Arthopyrenia (=Pyrenocollema)*, growing on
marble tombstone in Denmark, penetration of mycobiont hyphae in the base material
is very common (Bech-Anderson, 1986). These hyphae exhibited high content of
calcium, which understandable was derived from the substratum.

Gehrmann *et al.* (1988) investigated endolithic lichen flora of limestone and
sandstone used in Jewish tombstones in Germany and reported that many epilithic and
endolithic species of lichens penetrate up to a depth of ca. 15 mm in the stone.
Weathering patterns were in the form of pitting, etching, prints of fruit-bodies and
holes caused by penetration of mycobiont hyphae.

White crust of calcium oxalate at lichen substrate interface is formed when
*Dirina massilicensis f. sorediata* grows on rock (Seaward and Giacobini, 1991). This
crust filled major part of lichen thalline space. The lichen was seen covering large
parts of a temple column at Naples, Italy.

**Oxalate formation by metallic ions other than Calcium**

Some other metallic ions also produce oxalates by the action of biogenically
produced oxalic acid.
Magnesium oxalate has been found in the thallus of *Lecanora atra* (= *Tephromela atra*) growing on serpentine, a rock consisting of magnesium silicate minerals, particularly, chrysotile (Wilson *et al.*, 1980, 1981). Presence of dehydrated magnesium oxalate crystals called, glushinskite was observed at rock-lichen interface. The weathering product at the disintegrating rock face was an X-ray amorphous silica gel, that retained the fibrous structure of the original chrysotile but was devoid of magnesium upto the depth of 100 μm below the rock surface.

The thallus of *Pertusaria corallina* colonizing manganese ore was found to contain poorly formed, subsequent crystals of manganese oxalate dehydrate (Jones *et al.*, 1987; Wilson and Jones, 1984).

Several copper tolerant lichens were observed occurring on cupriferous substrates in Scandinavia (Purvis, 1984). On analyzing the thalli of *Lecidea lactea, L. inops*, and *Acarospora rugulosa*, vivid blue inclusions of copper oxalate encrusting the mycobiont hyphae of their medulla were found. Purvis (1984) believes that relatively insoluble oxalates of metals, such as, barium, cobalt, lead, manganese, nickel, silver and zinc may also be formed in thalli of lichens growing on mineralized rocks of appropriate composition.

**Other products than oxalates**

Some other products have also been reported to be formed at rock-lichen interface by action of oxalic acid. The weathering phenomenon of basalt by *Pertusaria coralline* is well known. This rock consists largely of two minerals; plagioclase feldspar (laboradprite) and ferromagnesian minerals. The latter one is often replaced by ferruginous clay minerals. The lichen by secreting oxalic acid
etches laboradorite and clay minerals to produce ochreus crust of ferruginous (ferrihydrite) and alumino-silicate materials (Jones et al., 1980, 1981).

The goethite containing aluminum was found in an ochreus deposit on the thalline surface of lichen Tremolecia atrata that colonized biotite-chlorite schist (Jones et al., 1981). Mycobiont hyphae of lichens also produce other simple organic acids, such as, citric, gluconic and lactic, by mycobiont hyphae of lichens (Caneva and Salvadori, 1988). These acids, like oxalic acid, react with metal cations.

**Chelation or complexing action of lichen acids**

Many of the lichen acids (also called lichen substances) have chelating property and are able to convert many minerals into water soluble complexes (Schatz et al., 1954; Schatz et al., 1956). These substances are effective chelators forming metal complexes with silicates (Seaward et al., 1989).

These so called lichen acids are mainly polyphenolic compounds that fall into two different series; 1. Aliphatic – containing fatty acids, polyols and triterpenoids, 2. Aromatic – containing tetronic acid derivatives, depsides, depsidones, quinons, dibenzofurans, and diketopiperazine derivatives (Hale, 1967).

Chelation is a chemical process and takes place when the reacting substances are in solution. In nature, water is omnipresent and acts as the universal solvent of innumerable substances. For a long time lichen acids were considered as insoluble in water. The presence of polar groups, viz., –OH, –CHO and –COOH in many of them, however, precludes the possibility of their total insolubility in water (Syers and Iskandar, 1973). Solubility of four depsides of orcinol series, e.g., erythrin, and evernic acid; and depside of β-orcinol series, e.g., 4-O-demethyl barbitic acid, squamic acid and atranorin, as well as six depsidones, barbitic acid of orcinol series,
and five, i.e., fumarprotocetraric acid, salazinic, norstictic, stictic, psoromic acids of β-orcinol series, commonly occurring lichen compounds ranging between 7-75 mg in a litre of water (Iskandar and Syers, 1971). This value though low, yet is significant for bringing about chemical reaction. The ability of a lichen acid for bringing out chelation of minerals depends probable more on their chemical structure rather than their solubility in water (Gehrmann et al., 1988). Presence of the aforementioned donor groups in ortho (adjacent) positions, i.e., -OH in evernic acid and salazinic acid, -CHO in atranorin, and -COOH in lobaric acid cause metal or cation complexing activity resulting in biological weathering of rocks (Gehrmann et al., 1988; Syers, 1969). On the basis of their molecular structure the lichen substances act as excellent chelators (Hale, 1967; Schatz et al., 1954). The lichenic acids also having metal complexing properties were studied by Bloomfield (1951), Davis et al. (1960), Iskandar and Syers (1972), Schatz (1963) and Swindale and Jackson (1956).

Water comes from the lichen thallus for carrying out chemical action in the process of chelation. It is absorbed by the lichen in liquid or vapour form (Gehrmann et al., 1988), and is retained in it even under extremely dry conditions (Smith, 1961). The medulla of the thallus thus acts as water reservoir (Smith, 1961).

As medullary zone of crustose lichens directly lies over the rock surface, chances of chemical rock weathering by them are manifold as compared to their foliose or fruticose counterparts. By water retaining capacity of lichen thalli against drying, the rock-lichen interface remains moist for longer periods, offering more time for carrying out of chemical reaction (Syers and Iskandar, 1973).

The mechanism of chemical reactions that cause rock weathering is well known (Saxena et al., 1991). The metabolites of lichens react with stone materials and decompose them either through salt formation or chelate formation. Monovalent ions
(Na⁺, K⁺, etc.) of stone minerals being replaced by protons are leached out by water movement. Bivalent or trivalent cations (Ca²⁺, Mg²⁺, Fe³⁺, etc.) are dissolved by chelate formation. The biogenically produced aliphatic carboxylic acids and aromatic phenolic acids chelate K, Na, Mg, Ca and Si of rocks.

Experimental evidence

*Parmelia consp era* reacted with mica and granite, producing reddish colour in 3-4 hours *Parmelia ptenophila* and *Umbilicaria arctica* reacted with silicate material, *Caloplaca elegans* (=*Xanthoria elegans*) showed no reaction (Schatz, 1963). Some extracted lichen acids, viz. physodic and lobaric acids also brought positive results with rock minerals. This was also observed in *Parmelia consp era* and also its chelating ability with that of fumarprotocetraric acid (Syers, 1969).

The Ca, Mg, Fe and Al in the silicate rock material of biotite, granite an basalt in aqueous suspensions were complexed by salazinic acid, stictic acid, evernic acid, lecanoric acid, roccellic acid and atranorin (Iskandar and Syers, 1972). Soluble complexes, generally coloured, were developed.

Using iron chelation as a measure for biochemical weathering of rocks, interesting experiments have been done (William and Rudolph, 1974) to determine the reaction of lichen acids produced by mycobionts and photobionts separately in cultures. The lichen species selected were *Caloplaca holocarpa, Lecanora dispersa, Cladonia cristatella* and *C. squamosa*. The photobionts showed zero activity in solubilization of iron except that of *Lecanora dispersa*, that too to negligible measure. Same was the case with the mycobiont of *Cladonia cristatella*. These experiments indicate to the probability that it is the whole lichen and not its symbionts separately that are capable of producing lichen acids responsible for any metallic binding
phenomenon. Production of lichen acids by any of the symbionts separately in *v* _v*iro* has not been confirmed (Culberson, 1969). Komiya and Shibata (1969), however, reported production of usnic acid and salazinic acid in mycobiont culture of _Ramalina_ species. In nature, within the lichen thallus where both the symbionts are in their usual self, there is a possibility of the photobiont producing a depside-hydrolyzing enzyme yielding phenolic components of lichen substances, many of which could act as chelating agents (Schutz and Mosbach, 1971).

4-0-demethylbarbatic acid has been isolated from the cultured mycobionts of two strains of _Ramalina siliquosa_, which in lichenized state produces salazinic and protocetraric acids. Schutz and Mosbach (1971) considered that perhaps the photobiont brings about the oxidation of the former, resulting in the end products of the lichenized state. 4-0- demethylbarbatic acid has also been isolated from mycobionts of _Ramalina subbreviuscula_ and _R. subcomplanata_. The former species in lichenized state contains salazinic and divaricatic acids and the latter salazinic and sekikaic acid derivates; sekikaic, homosekikaic, and 4-0 methylnorhomosekikaic acids. 4-0- demethylbarbatic acid is probably the precursor of salazinic acid and the photobiont plays the role of oxidizing the former, producing β-orcinol depsidone, but regarding end products of _R. subbreviuscula_ and _R. subcomplanata_ it was difficult to ascertain experimentally that their precursor was 4-0 demethylbarbatic acid.

_Parmelia conspersa, Rhizocarpon geographicum_ and _Umbilicaria pustulata_ are more effective in inducing colour complex changes than are four tested lichen substances (atranorin, stictic acid, usnic acid and norstictic acid) singly or in combination (Ascaso *et al.*, 1976). It is perhaps due to presence in thallus of selected species of substances allied to gluconic and galacturonic acids or some other compounds that are exhorted by non-lichenized fungi.
Certain rock silicates do not only become structurally modified by the action of lichen acids but also give rise to new minerals under natural conditions. Two types of acidic rocks, granite and gneiss were studied and observations made on the nature of minerals at rock-lichen (*Rhizocarpon geographicum*, *Parmelia conspersa*, and *Umbilicaria pustulata*). Edges and surface of mica and feldpars were altered and presence of amorphous silica, twinned goethite crystals (-FeOOH), hallosite and kaolinite was noticed. These observations demonstrate the ability of lichens to bring about chemical and morphological changes in rocks under natural conditions.

Chelating properties of salazinic, stictic, evernic, lacanoric and roccellic acids as well as atranorin has been demonstrated by making them react with aqueous suspensions of biotite, granite and basalt forming generally coloured complexes (Caneva and Salvador, 1988).

**Optical and analytical observations**

Hypha was detected in quartz grains at thallus of *Dimelaena oreina* rock interface (Halbour and Jahns, 1977). This species was found to contain stictic, constictic and usnic acids, as well as some accessory substances. SEM and EDX investigations revealed that the hyphae not only penetrated the micaceous matrix but also attacked quartz, indicating chemical boring of this substrate.

The action of four lichen compounds, namely, atranorin, fumarprotocetraric acid, usnic acid and stictic acid on sandstone, basalt, marble and limestone has been estimated (Gehrmann *et al.*, 1988) through SEM photographs, presented disintegrating pattern on surfaces of marble and limestone but none of the four substances appeared to bring about any change in sandstone and basalt.
Effect on cultural heritage

*Parmelia tinctorum*, a foliose lichen growing on large areas of the Buddhist monument at Borobudur, Central Jawa, was found defacing sculptured panels. This lichen contains an unusually high percentage (20.3) of lecanoric acid, a substance that is well known as chelator of metallic ions (Seshadri and Subramanian, 1949).

Weathering of a granite statue by lichen growth has been reported from India (Gayatri, 1980). By analysis of trace elements in the granite and also their uptake by lichens (*Parmelia grayana* and *Roccella montagnei*) it was demonstrated that their thalli exhibited selective enrichment of lithium, sodium, potassium, zinc, lead and cadmium.

Effect of lichens on rock forming minerals varies according to their chemical composition and crystallographic structure (Jones et al., 1987).

Generally carbonate and ferromagnesian silicate minerals weather easily, leading sometimes to total decomposition. Widespread corrosion starts appearing right from early stages of weathering in case of magnesian minerals. Crustose lichens produce weathering symptoms, like deep etch pits in olivine grains, and deep cross-cutting trench-like mards on the surface of augite grains. The latter probably represents the weathering out of exposed lamellar ingrowths of slightly different chemical composition (Jones et al., 1981).

Extraction of cations, e.g., Mg, Fe, K and Al from biotite results in substantial changes in its structure in which a coherent siliceous relect is left behind (Wilson and Jones, 1983).

In the likewise manner, chrysotile, a fibrous magnesium silicate mineral may be changed to an X-ray amorphous silica gel without disturbing the fibrous structure to the original material (Wilson et al., 1981).
In case of feldspars, lichen activity shows much less effect on their surfaces, but sometimes they too show symptoms of weathering caused by lichens. One of the varieties of this group of minerals, anorthite, that is rich in calcium, easily gets reduced to an isotropic, siliceous pseudomorph. Laboradorite and albite, two other kinds of plagioclase feldspars exhibit extensive corrosion of lamellar inter-growths or develop diamond-shaped etch pits by activity of lichens. In K-feldspar corrosion by this group of plants is to a lesser extent.

Lichens do not seem to be very successful in making inroads in weathering of quartz. Yet, this rock sometimes yields to biogeochemical weathering caused by lichens. Etching of highly quartzite surface by *Dimelaena oreina* is known (Halbaur and Johns, 1977). Corrosion of quartzite substratum colonized by lichens is also reported (Jones *et al*., 1981).

The common lichen substances well known for their metal complexing properties are listed by Shibata (1964).

1. Higher fatty acids

   Roccellic acid

2. Phenolcarbolic acids

   A. Orcinol derivatives

   a. Depsides

   Erythrin

   Evernic acid

   Lecanoric acid

   b. Depsidones

   Barbatic acid

   Physodic acid
B. β-Orcinol derivatives
   a. Depsides
      Atranorin
      4-0-demethylbarbatic acid
      Squamatic acid
   b. Depsidones
      Fumarprotocetaric acid
      Norstictic acid
      Psoromic acid
      Salazinic acid
      Stictic acid
   c. Pholoroglucinol derivatives
      Usnic acid

3. Amino acid origin of uncertain position constictic acid

In general the role of physical and chemical agencies in the weathering of rocks and minerals has been adequately documented by both geologists and pedologists across the world.

Generally, rock surfaces are not regarded as being particularly conducive to the growth and development of living things. Occasionally, grasses or forbs or even, more rarely a small shrub or stunted tree growing from a crack in large boulder or rock wall may be encountered. But by most people, rock is perceived as dry, sterile, impenetrable and generally uninviting. However, to the experienced eye rock surfaces is often teeming with life—lichens, bryophytes, a host of small, invertebrate animals, as
well as a vast array of microscopic organism including bacteria, cyanobacteria, algae and non-lichenized fungi.

Lichens are eminently successful and enjoy a world wide distribution. They occur in every conceivable habitat and in more than few cases play a central role in the operation of some natural systems, growing on a variety of substrata, including most natural substrata as well as a host of human manipulated or manufactured substrata. Common natural lichen substrata include all categories of rocks and bark, decorticated wood, decomposing wood, living and dead branches of trees and shrubs, evergreen leaves, cactus spines, exoskeletons of insects, bleached bones, and both mineral and organically enriched soils. Common manmade substrata supporting lichens include rubber, plastic, glass, stonework, concrete, plaster, ceramic and terracotta tiles, bricks, processed wood products, cloth, canvas and various types of metals.

Biodeterioration of historical and culturally significant stone substrates is a complex problem. The biodeterioration issues are multidisciplinary where biologists join with ecologist, geologists, geochemist, crystallographers, cultural conservators, archaeologists, anthropologists and historians. In the last 3-4 decades of the last century studies regarding Lichen and biodeterioration of stone surfaces has gained interest across the world. The different studies can be categorized into following aspects-

- Biodeterioration of Monuments - general studies; floristic, vegetational and ecological studies on lithic substrata; lichens as deteriorators of stonework; lichen substratum relationship.
- Degradation of rocks and stonework by lichens; weathering processes due to lichens as biogeophysical and biochemical agents.
- Oxalate patinas.
- Methods for prevention and control of lichen colorization on monuments.
- Biomonitroing and heritage buildings.
- Aerobiology and heritage buildings.
- Critical bibliographies and reviews on lichens and biodeterioration of rocks and stone work.

**Indian scenario**

There are only few reports of lichen induced damage to Indian monuments are available. It was Gayathri (1980) for the first time described the effects of lichens on granite statues in India.

Singh and Uperti (1991) provided a detail account of lichens growing on different monuments of the Lucknow City and listed the occurrence of eleven species of lichens.

Singh and Dhawan (1991) studied the qualitative assessment of damage caused by three lichens species to a 16th century stone monument, Yognarsimha Swami temple, Baggavalli, Karnataka. On account of molecular structures of the lichen acid present in different lichens, interesting observations on stone weathering of monuments is also provided.

Chatterjee et al. (1996) enumerated 18 genera and 40 species of lichens from some Indian monuments in Karnataka and Orissa. Taxonomic account and key for their identification was provided. The monuments exhibit a distributional pattern of lichens depending on microclimate create at different niches by their architectural designs.
Chatterjee et al. (1996) listed the lichen species occurring on some Indian monuments in eleven districts of Karnataka, Orissa and Uttar Pradesh. The lichen distribution and frequency of lichens over monuments seems to be controlled by the prevailing climatic conditions and architectural patterns of the monuments.

Upreti (2002) studied the lichen flora of Khajuraho group of temples and rocks of near by areas and listed the occurrence of 10 taxa of lichens. It was observed that the type of stone, architectural design and climatic conditions determine the composition of the lichen flora. The walls near the ground level were more shaded and moist, bears the luxuriant growth of some moisture loving lichen species of *Endocarpon*, *Buellia* and *Peltula*.

Singh and Sinha (1993) provided a detail account of the corrosion of natural and monumental stone with special reference to lichens, the kinds of rock damages, together with list of lichen substances was provided.

Bajpai et al. (1992) suggested a fast technique for investigating the effect of biocides on lichens. The technique is based on the measurement of the total number of ultra weak photons emitted by living systems in the visible range. The individual organism, such as thalli of algae, fungi or lichens etc., or any part of it or of other groups of plants in the form of living tissues emit ultra weak photons. The flux of which exhibits an interesting structure lasting for a few minutes. The structure a light induced and reproducible can characterize the metabolic activities of a system. As it a characteristic property of *in vivo* material only, it can be used to estimate the relative amount of living and dead material in a sample. It can thus be used to quantify the efficacy of various biocides on different organisms. Bajpai et al. (1992) used to estimate the effective dose of a few biocides on a single species (*Parmelia tinctorum*)
of lichen in order to eradicate it from the monuments of which it grows and causes damage.

Bajpai et al. (1999) used the same technique to study the effect of some other biocides on some other lichen species. The biocides used were mostly the agricultural biocides. The butachlor and the propachlor are two promising pre-emergence herbicide. Of the two herbicides, propachlor is a propanil. The former is known to interfere in protein synthesis while the latter interfere in DNA and protein synthesis as well as blocks the Hill reaction in photosynthesis. According to Anderson (1978) these herbicides also have the anti-fungal and anti-algal properties in certain concentrations and under specific soil conditions.

Bajpai et al. (1999) observed that a single treatment with 5% Butachlor, 5% Mancozeb, 2% Tridemorph, or 1% Simazine is sufficient to eradicate the lichen species Pertusaria velata, Lecanora sp., Thelenilla sp., Diploschistes scruuposus, Cladina aggregata, Cladonia calycantha and Heterodermia.

Chatterjee and Singh (1999) provided a detail review on the lichens and monuments, also listed the factors affecting growth of lichen establishment on monuments and Lichen-monument relationship.

Singh et al. (1999) described the details of the 40 lichens species belonging to 18 genera and 14 families, found growing on certain monuments of Karnataka and Orissa. For eradication of the lichens from monuments, detail of the chemical treatment was also provided. Twelve laboratory chemicals and agricultural pesticides, herbicides and fungicides were tested. Crustose lichens were found to be the most resistant to chemical treatment, followed by foliose and then by fruticose forms. Some chemicals such as paraquat dichloride, polycide and butachlor impart their own
colours to stone materials. They must, therefore be rejected for conservational purposes.

Jain (2001) listed for species of algae and lichens found growing on Gwalior Fort in Madhya Pradesh.

Upreti et al. (2004) studied the lichen activity over rock shelters of Bhimbetka world heritage zone, Madhya Pradesh. A total of 14 species of lichens growing over rocks in different localities of the area were listed together with their thallus character and chemical products. The approach for carrying out lichenological studies together with the potential of lichen activity over rocks is also discussed.

Saxena et al. (2004) provided a detailed account of lichens growing on different artifacts in the Indian subcontinent. Some interesting distributional and ecological patterns of lichens growing on historical monuments and building were also presented.

Garg et al. (1995) summarized the state of knowledge with regard to the role of fungi in the deterioration of wall paintings in different parts of the world. Factors conducive to fungal growth on wall paintings, fungal flora on wall paintings, effects of fungal growth on wall paintings, mechanism of decay, methodology used for the study of fungi and control of fungal growth on wall paintings was also discussed in detail.

Mishra et al. (1995) reviewed the present status of knowledge on the role of higher plants in the deterioration of historic buildings in India. Factors conducive to the growth of higher plants, deterioration caused, control measures for higher plants growing on Indian monuments and their detailed enumeration was also presented (Table 1).
Table 1: Higher plants growing on Indian Monuments

<table>
<thead>
<tr>
<th>No.</th>
<th>Plant</th>
<th>Local/common name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pteridophyta</td>
<td>Dryopteris sp.</td>
</tr>
<tr>
<td></td>
<td><strong>Dicotyledons, woody</strong></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td><em>Acacia arabica</em></td>
<td>Babul</td>
</tr>
<tr>
<td>3</td>
<td><em>Albizia lebbeck</em></td>
<td>Siris</td>
</tr>
<tr>
<td>4</td>
<td><em>Azadirachta indica</em></td>
<td>Neem</td>
</tr>
<tr>
<td>5</td>
<td><em>Dalbergia sisso</em></td>
<td>Shisham</td>
</tr>
<tr>
<td>6</td>
<td><em>Ficus bengalensis</em></td>
<td>Bhargad</td>
</tr>
<tr>
<td>7</td>
<td><em>Ficus religiosa</em></td>
<td>Peepal</td>
</tr>
<tr>
<td>8</td>
<td><em>Holoptelea intigrifolia</em></td>
<td>Chilibill</td>
</tr>
<tr>
<td>9</td>
<td><em>Zizyphus jujuba</em></td>
<td>Ber</td>
</tr>
<tr>
<td></td>
<td><strong>Dicotyledons, herbaceous</strong></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td><em>Argemone maxicana</em></td>
<td>Bharband</td>
</tr>
<tr>
<td>11</td>
<td><em>Boerhavia diffusa</em></td>
<td>Creeping spindering</td>
</tr>
<tr>
<td>12</td>
<td><em>Calotropis procera</em></td>
<td>Madar</td>
</tr>
<tr>
<td>13</td>
<td><em>Cassia occidentalis</em></td>
<td>Sicklepod</td>
</tr>
<tr>
<td>14</td>
<td><em>Coccinia indica</em></td>
<td>Wild Kunaro</td>
</tr>
<tr>
<td>15</td>
<td><em>Convolvulus sp.</em></td>
<td>Field wind weed</td>
</tr>
<tr>
<td>16</td>
<td><em>Croton bonplandianum</em></td>
<td>Croton</td>
</tr>
<tr>
<td>17</td>
<td><em>Datura sp.</em></td>
<td>Dhatura</td>
</tr>
<tr>
<td>18</td>
<td><em>Eclipta alba</em></td>
<td>Bhangra</td>
</tr>
<tr>
<td>19</td>
<td><em>Euphorbia hirta</em></td>
<td>Spurge</td>
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<tr>
<td>20</td>
<td><em>Heliotropium indicum</em></td>
<td>Heliotrope</td>
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<tr>
<td>21</td>
<td><em>Mimosa pudica</em></td>
<td>Sensitive plant</td>
</tr>
<tr>
<td>22</td>
<td><em>Oxalis sp.</em></td>
<td>Creeping wood sorrel</td>
</tr>
<tr>
<td>23</td>
<td><em>Physalis minima</em></td>
<td>Ground cherry</td>
</tr>
<tr>
<td>24</td>
<td><em>Sida cordifolia</em></td>
<td>Sida</td>
</tr>
<tr>
<td>25</td>
<td><em>Solanum nigrum</em></td>
<td>Black nightshade</td>
</tr>
<tr>
<td></td>
<td><strong>Monocotyledons, herbaceous</strong></td>
<td></td>
</tr>
<tr>
<td>26</td>
<td><em>Agropyron repens</em></td>
<td>Quack grass</td>
</tr>
<tr>
<td>27</td>
<td><em>Cynodon dactylon</em></td>
<td>Bermuda grass</td>
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<td>28</td>
<td><em>Cyperus rotundus</em></td>
<td>Nustage</td>
</tr>
<tr>
<td>29</td>
<td><em>Imperata cylindrica</em></td>
<td>Congograss</td>
</tr>
<tr>
<td>30</td>
<td><em>Saccharum munja</em></td>
<td>Tiger grass</td>
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