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DETERIORATION PROCESSES OF HISTORICAL MONUMENTS

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ABSTRACT

The problem of the conservation of historical monuments (statues, columns, ancient buildings) requires an accurate study of the many environmental agents which bring about the deterioration process and affect the actual rate of deterioration. Among the most active causes of weathering, we can cite: (i) the weakening of the outer layer of the art work, which is caused by complex microphysical effects and is in particular due to wetting of the monument (a comparison between the effects of rainwater and condensation is made); (ii) the chemico-physical action of pollutants captured in both the dry and wet phase. The destructive processes depend on many factors: the past history of the monument, the capture and nature of the pollutants, and the frequency of some microclimatic conditions, particularly those supplying the water necessary for chemical reactions. To this end studies of diurnal and seasonal variations on the monument of both the heat wave and the fluxes of moisture and energy are very important.

Some of these processes have been shown with microclimatic studies and microphysical investigation associated with mineralogic and chemical analyses of samples of weathered material. Mathematical models in some cases (especially for solar radiation and temperature) permit physical simulation, reconstruction of past data and extrapolation into the future observation of many monuments from different epochs; situated at various sites, gives examples of the fundamental processes that are often associated with, or masked by, other effects.

The main weathering processes are due to the combined action of rainwater and atmospheric pollutants (particularly the carbonaceous particles due to combustion) deposited on the surface of the monument. The way in which the surface is wetted is very important: in fact, a short drizzle can activate the dry deposit without washing it away, and in this case the pH of rain droplets is of secondary importance; on the other hand, showers supply abundant water which favours dissolution of the stone and removal of the solute, resulting in a thinning of the original rock. Another important factor is the dynamic regime (i.e. laminar or turbulent) of the water flowing over the surface of the monument.

In zones where the surface of marble or calcareous monuments is only wetted, but protected from run-off, black crusts (characterized by crystals of gypsum and calcite with carbonaceous particles embedded in the crusts) are formed. Zones subjected to heavy run-off are also subjected to a thinning of the rock and small authentic calcite crystals form that are white in

appearance.

In the case of relatively unpolluted towns, where marble and limestone sulphation is not the main cause of the deterioration process, biological deterioration mechanisms are often very important, due to the activity of epilithic and endolithic microflora and microfauna.

The case of particularly precious mortars, i.e. murals or frescoes, is discussed in order to clarify the thermodynamic method proposed for the analysis of experimental campaigns. Finally actions are described that act on the causes and not only on the effects.

CAN DETERIORATION BE EXPRESSED IN TERMS OF SULPHUR DIOXIDE LEVELS OR ACID RAIN ALONE?

In the last decade, Europe has witnesed a progressive deterioration of its inestimable artistic heritage and the definitive loss of many masterpieces. It is clear that the cause of this calamity is linked to the by-products of our modern society, and in particular to atmospheric pollution, but it is not particularly clear which chemical components are the most directly responsible , or exactly how they act on the monuments (statues, ancient buildings, columns, etc.). As the rate of monument deterioration has occurred with the general increase in both industrialization and urbanization, especially after the second world war, many authors suggested that this phenomenon could be ascribed to the increasing rate of air pollution and in particular to sulphur dioxide (for an overview see ref.1).

In this hypothesis the deterioration process is mainly due to the surface action of sulphur pollutants removed from the atmosphere by condensation processes (ref.2). The corrosion of marble and limestone would be due to the transformation of sulphur compounds , in particular of sulphur dioxide in the presence of catalysts into sulphuric acid on the surface of monuments. With this model we would expect to find buildings and statues weathered in a more or less uniform way, with only one kind of deterioration crust, thicker or thinner according to the environmental aggressivity, which could then be simply expressed in terms of concentration of pollutants in the atmosphere and time of wetness, the time during which and adsorbed film is present on the surface. As a consequence, we would expect to find monuments more severely deteriorated and covered by a thicker and continuous scab on the northern side, which is the more humid part of a monument, similar to trees covered by moss. This model fails on three points: (i) not one reliable quantitative correlation has been found between sulphur dioxide (or other pollutants) concentration and damage; (ii) the location of scabs on the monuments is not in accordance with this hypothesis; (iii) on the same monument we can find sulphated areas and non-sulphated areas, exposed to the same concentration levels of atmospheric pollutants during the same period of wetness.

Acid rain was indicated as another possible cause of stone deterioration (see e.g. ref.3). Many studies have been carried out in this direction with contradictory results. If we observe a monument, we can see that, the parts more exposed to the damage caused by rain, i.e. those experiencing run-off, have deteriorated in a different manner from those protected from run-off. The proposed weathering process has, in practice, three steps: (i) atmospheric gases dissolved in water form a chemically active solution; (ii) this reacts with the stone and forms the crust, transforming part of the calcite of the statue into gypsum, which is more soluble in water; (iii) the next rainfall washes away the crust removing a layer of stone (ref.4). The loss of material is a function of both the the pH, considered as an index of the aggressivity of rainwater, and the intensity of rainfall (ref.5) which supplies a new unsaturated solution in contact with the surface. The process would be more active if the precipitation occurred on already damp stone.

In reality, on marble monuments the zones experiencing run-off are thinned. Only rarely does the precipitation of a thin layer of spatic calcite occur. Surprising, considering the above mentioned step (iii), sulphation is hardly present. When run-off is prevented, sulphation is at its maximum. Therefore, one must conclude that: (i) a noticeable part of sulphur compounds that affect the stone are airborne and deposited via dry deposition processes; (ii) the main action of the acid rainfall is to thin the stone, but acid rainfall alone is not sufficient by itself to explain the formation of one of the worst kinds of stone deterioration: the formation of the well known black crusts, essentially composed of gypsum crystals and soot particles.

The role of chemical agents has been extensively studied since the problem first arose, many problems , however, remain still unsolved. One could suppose that both sulphur dioxide and acid rain are partially responsible for stone deterioration, but to what extent it is not easy to say. They are only part of a more complex process.

In the case of relatively unpolluted towns, where marble and limestone sulphation is not the main cause in the deterioration process, biological deterioration mechanisms may be very important. The most active plant organisms found in the Mediterranean region are blue algae and lichens; and the animal organisms are mainly rotiphera (ref.6 and 7). The increase of environmental pollution levels has caused a change in the biological activity: epilithic species have been progressively substituted by endolithic organisms as these are more compatible with the new habitat.

Careful observation of weathered monuments reveals that deterioration is not only due to chemical and biological agents but is also a function of: local microclimatic conditions, of porosity which continues to increase with exposure (ref. 8) and of surface geometry.

The effects of microclimatic factors (see ref.9 to 12) and surface geometry have not been widely studied. The aim of this paper is to emphasize the influence of these two hardly known factors and conclude with a general model on the formation of the different crusts and visual features of weathered carbonatic limestone. We will speak in general in terms of stones, but all the problems associated with the porosity of limestone can also be extended to bricks and mortar. Special reference is made to limestone and marble, as the main monuments of the Mediterranean basin, from the classical Roman and Greek age, to the Gothic, the Renaissance, the Baroque epochs, are made from these materials.

THE ROLE OF THE MAIN MICROCLIMATIC FACTORS

Solar radiation causes the heat and moisture exchange between the atmosphere and the monument. It is well known that a variable input of heat causes thermal gradients and mechanical stress inside the monument, which can reach undesired levels near the juncture zones, e.g. legs of a bronze equestrian statue imprisoned a marble base, or bronze panels nailed onto a wooden door as in the many Gothic and Renaissance buildings. The zones weakened by severe stress may be more exposed to the risk of further weathering. Broad temperature cycles may enhance mechanical damage, especially when they are associated with an undesired hygrometric effect. Experimental field tests on the seasonal and diurnal environmental cycles combined with mathematical models to describe general problems on specific monuments, have permitted the physical simulation, the reconstruction of data and a prediction for the future, such as in the case of the San Marco Horses in Venice or the Trajan and Aurelian Columns in Rome and several other Basilicas (ref. I3 to 2I).

Fluxes of heat and moisture can favour or oppose the deposition processes of atmospheric pollutants and the adsorption of gases. For example, in Rome we found that the hourly sulphur dioxide concentration has a bi-modal diurnal distribution, but the effects of one of these two peaks should be considered negligible. In any case, the deposition rate is a function not only of the concentration of pollutants in the atmosphere, but also of different deposition processes, that are in itself a function of both atmospheric and surface characteristics. Moreover these processes are generally unknown. This explains how hazardous it would be to make a correlation between pollutant concentration in the atmosphere and the resulting damage to the stone.

The diurnal thermal cycle of the monument associated with the variation of the environmental specific humidity, may cause condensation-evaporation cycles on the stone surface, which in turn depend on the stone temperature, presence and kind of soluble salts and the dew point of the environmental air. Clearly, it is not correct to consider only the relative humidity of the surrounding atmosphere in order to make a model of this process. Less known but much more frequent are condensation-evaporation cycles on micropores. Condensation on external micropores occurs at lower equilibrium relative humidities with respect to a flat surface, favoured by the variation of the saturation vapour pressure over a meniscus (according to the Kelvin equation) and evaporation occurs symmetrically. In the internal micropores condensation depends in addition to the above parameters, on the spatial association, geometrical shape and the radii of curvature of the micropores. Evaporation depends on the radius of the pore outlet (ref.22, 23). Therefore, considering only one waterfront inside the monument is a very crude approximation of the reality: one should consider a series of waterfronts in spatial succession in the stone, each one dependent on kind and critical values of the pores which become filled with water at that depth.

Not only direct solar radiation causes spatial differences in the surface temperature; also during the night, the infrared radiative loss (which is greater for horizontal surfaces which face the sky than for vertical ones) and the heat supplied by conductivity from the interior (this must be considered for a non homogeneous monument) lead to more moderate temperature dishomogeneities. The risk of condensation is higher towards the end of the night and early in the morning, when the specific humidity in the atmosphere rises and the temperature of some shaded parts of the monument doesn't rise above the dew point of micropores and surface, due to the thermal inertia of the monument. This is not the only way to fill micropores: rising groundwater and rainfall are very effective in making buildings and statues damp, thus accelerating spalling, exfoliation and formation of deterioration crusts.

Water in micropores is responsible for many undesirable effects:

i) dissolution of some crystalline bondings and weakening of the mechanical resistence; recrystallization of the solute with new chemico-physical properties when evaporation occurs (see Fig.1). This process results in weakening the stone and in reducing its transpiration capacity, which may lead to severe deterioration (ref.24) such as surface microfractures, exfoliation, spalling and sugaring;

ii) transport of soluble salts through the stone, mainly due to rainfall, capillary rise of ground dampness, evaporation; then efflorescences and subflorescences, obstruction of capillary outlets;

iii) overpressure inside the porosities and capillary fringe when liquid water evaporates and the outlets are obstructed (as the ratio of the molar volumes of liquid water and vapour is 18:22400). However, evaporation (and this potentially distructive pressure) is controlled by the limited diffusivity of water vapour inside the pores and capillary system. However, a moderate but frequent overpressure may result in the flaking off of deteriorated surface layers;

iv) wetting-drying cycles. Wetting is mainly due to rainfall, capillary rise, condensation; drying is due to evaporation. In general, a lot of deterioration phenomena can be related to the frequency of wetting-drying cycles of whatever origin, which involve dissolution, migration and recrystallization of soluble salts, as we will see below;

v) freeze-thaw cycles in cold regions;

vi) endolithic or epilithic biological activity.

The wind is responsible for many actions on a monument: it affects the temperature pattern especially of evaporating surfaces; it is responsible for different types of wetting of the monument, furnishing a horizontal component to the velocity of falling drops and causing preferential paths to the run-off; it induces the removal or deposition of airborne particles; it may cause abrasive weathering in the zone close to the ground; it causes mechanical stress; it may favour the loss of pieces already very loose (ref.25).

Evaporation caused by wind transporting unsaturated air masses may have a different effect from evaporation caused by solar energy heating the monument. Wind plays a very important role in increasing the evaporation rate, which is associated with the transport through the stone of liquid water containing dissolved salts, and recrystallization where evaporation has occurred. Wind caused evaporation occurs typically on the surface of damp walls and therefore is effective in the transporting of salts to the surface and forming efflorescences, as in Venice, in a very humid environment, where the buildings are only rarely hit by solar radiation. Of course the efflorescences are more developed in the more ventilated zones, such as corners etc. When the surface is no longer supplied with water from capillaries, the evaporation rate drops since evaporation now occurs in the inner pores, and wind favours the slow diffusion of water vapour and the continuation of the process. When evaporation occurs deep inside the stone, the salts dissolved in the evaporating water crystallize in the stone interior. In this case the mechanical structure remains weakened but in a minor manner and efflorescences are not formed, thus reducing the probability of exfoliation. If during the night condensation does not occur, the efflorescences remain on the surface and can be periodically washed away by rain. In the case of regular condensation during the night (as in Venice), the external efflorescences can migrate again into the outer layer of the damp walls, accelerating the distructive process.

Solar radiation supplies energy to the stone and the liquid water on the surface and inside, so that evaporation may occur also in the internal micropores when the temperature of the wall raises the internal relative humidity over critical levels which locally depend on the complex geometry of the pores and their outlets. The factor limiting this process is the low diffusivity of water vapour through the pore and capillary system, which can be increased by wind action. The low diffusivity tends to raise the internal relative humidity and stops evaporation when new water vapour is added to the internal atmosphere. However, the increase of the pressure within the capillary and porous system caused by the warming of the internal atmosphere, displaces part of the liquid water which is in their necks, out of its original position, so that a small portion may also be forced outside the stone in its liquid phase (ref.23). The evaporation occurring in the interior stone is less dangerous, as we have already seen.

Another noticeable effect of the wind is associated with its gusty character (and with the instability generated by eddies formed on the monument to a lesser extent), which alternatively causes rapid over and underpressures between the air inside the porosities and capillaries, and the air external to the monument, so that a net alternating force is applied to the surface. This tends to detach superficial layers poorly attached , that have a reduced transpiration capability.

During rainfall the fluctuations in the external pressure and the dynamical impedance of pores and capillaries cause alternating pressure gradients between the stone surface and its interior. This effect, associated with the sink effect of internal porosities results in a net transport and trapping of external water inside the monument. Capillary suction of the water on the surface of monuments is another mechanism for rainwater penetration.

Long term dynamic variations of pressure, as occur locally due to a disturbance in the mean wind field as caused by an obstacle, can be effective in varying the rise of ground dampness, since the induced pressure gradient increases or opposes the effects of capillarity and osmosis. These long term pressure gradients across walls make a negligible contribution in favouring or opposing penetration of rainwater through stone and mortar, but may be important in the case of cracks.

In polluted regions the wind is a very important factor in transporting and diffusing airborne pollutants.

Rainfall is one of the most important meteorological agents, especially when it is associated with wind. Protrunding parts of monuments (like an arm) and lower parts of buildings are less exposed due to the deflection of the wind field transporting falling droplets. Apart from the transport of heat and momentum, rainfall is responsible for supplying large amounts of liquid water, which cannot be supplied by means of condensation. The amount of water supplied by precipitation causes run-off or may only wet the surface, depending on wind speed and direction, local topography, exposure and geometry of the surface. The water supplied, when associated with aggressive chemical agents, may provoke chemical reactions and the dissolution of the stone.

The dynamic regime of the water flowing over the stone is important. In the zones characterized by a laminar regime the loss of material is less than in zones with a turbulent flow, where mechanical and chemical activity (due to the mixing of water in contact with the stone) are increased. In highly porous stone, run-off is progressively attenuated by the suction of water, so that the upper part of the descending stream, which has abundant water in a turbulent regime, is very efficient in dissolving the stone and removing material; the lower part in a laminar regime deposits the material previously removed; finally the stream disappears after the suction of the running water.

Rainfall intensity is also important. Drizzle may activate the dry deposit without washing it away, as in the case of heavy showers. In this case the pH of rainfall is clearly of secondary importance, compared with the acidity deriving from the dry deposition. Quantitative field measurements show that the loss in weight of the limestone samples varies according to the geometry and exposition both of which determine the total amount of water running over the surface.

Frequency and seasonal distribution of rainfall are important factors in the maintenance of the water content in bricks or stones, which is essential in the case of some biological or chemico-physical weathering.

Condensation-evaporation cycles in the micropores are important due to their frequency which can eventually contribute to the increase in the deposition processes and weathering. Condensation first occurs in the cavities with smaller radii, the larger pores retain their air, the outlets being obstructed by condensed water, like a bottle turned upside down and immersed in water. Thus, further condensation is prevented. The process continues when a variation in pressure (induced by wind gusts or by a variation in the temperature of the stone) forces the water out of its original position to be trapped in the next, larger pore (ref.23). External condensation, followed by capillary suction brings about a greater degree of damping of the stone. However, due to the condensation in the smaller bottlenecks, the air pockets in the interior of the capillary system may stop this process.

Phoretic transport of airborne pollutants and their capture on the stone surface are regulated by condensation. However, condensation is less important than rainfall in the deterioration process, as can be seen if zones exposed to condensation but protected from rainwater, are compared with zones exposed to both. The reason is that, in general, condensation supplies an insufficient amount of water for the formation of an aggressive solution (a heavy dew forming on an horizontal surface is about 0.5 mm per night, and is much less on vertical surfaces). Condensation is mainly active on the lower part of the stone monuments with poor porosity, where the largest drops running along the surface collect. More often condensed water is gradually absorbed by the dry deposit, the external weathered layer and the inner porosities, so that severe deterioration processes are not triggered. Under loggias, porticos, terraces where direct rainfall or windborne droplets do not arrive, we see that the stone is well conserved, demonstrating that condensed water is not sufficient to trigger severe physico-chemical deterioration, unlike what is popularly belived.

Condensed water may be sufficient to sustain biological activity, especially in periods of scarce precipitation.

Wetting-drying cycles induce severe weathering. Steady-state conditions would be highly desirable. It is obvious that for porous materials the least convenient environmental levels of relative humidity are those in which small variations in the relative humidity cause the greater difference in the water adsorbed by the statue. This occurs most often at intermediate humidity levels. Therefore extreme values are preferred. However, near-saturation conditions may be conducive to biological attack, and the work of art risks severe efflorescences. Drying causes significant mechanical damage, especially when this occurs at a high rate. Still water, may conserve an artifact without raising serious problems. These arise when part of the material can be dissolved, and this occurs typically when the body is immersed in, or water flows over it. In general the best conditions are found in steady, dry environments.

Freeze-thaw cycles are less frequent than condensation-evaporation cycles in the Mediterranean region, but the mechanical structure may be subjected to stress thus causing surface scaling, exfoliation and cracking. The damage is generally greater for materials having small porosities. Hoarfrost is not responsible for this kind of damage. Hoarfrost is a deposit of ice crystals by direct sublimation on objects with temperatures below freezing. The critical temperature, i.e. the frost-point, can be calculated as a function of the environmental specific humidity by means of the Magnus equation. When the moisture content in the atmosphere is very low, saturation occurs at below zero temperatures, but saturation with respect to ice occurs at a higher temperature than saturation with respect to supercooled water, so that in practice we see the formation of hoarfrost and not of supercooled dew. Hoarfrost in pores is not a dramatic event, since direct sublimation occurs at very slow rates and the growing ice crystals occupy only a small part of the free space in the microcavities, as the disposable vapour is very limited and its supply from the external atmosphere is negligible. Deterioration occurs in the case of frozen dew, i.e. when the temperature of the stone descends below the dew point of the micropores, so that they can fill with water, and then successively below zero. The larger pores which rarely become filled with water, are less exposed to this risk.

Snow deposited on stone has been recognized as inhibiting sulphate precipitation; it washes out sulphuric acid and eventually leads to the precipitation of calcium carbonate (ref.26). The effect of wetting the underlying stone during the melting sequence is more dangerous, as this water in the stone may be subject to freeze-thaw cycles, thus inducing crioclasticity.

In humid environments with very low or low pollution levels, biological weathering results on a thin surface layer (a few hundred microns). Among a wide series of biological processes, special attention should be given to the activity of algae, fungi and lichens. As a result of their action, the precipitation of calcium oxalates (weddellite and whewellite) has been found in some cases (ref.6, 7)

By means of microclimatic studies and microphysical investigation associated together with mineralogic and chemical analyses of samples of weathered material, part of the above processes have been analyzed. Observation of many monuments from different epochs and situated in various sites, has thrown light on these fundamental processes, which are often associated with, or masked by, other effects.

COMBINED ACTION OF POLLUTANTS AND RAINFALL

In this century air pollution has changed not only quantitatively, but also qualitatively. High pollution levels already existed before the present time, as we can judge from past regulations (ref.27, 28, 29). However, high concentrations of carbonaceous particles due to the combustion processes (especially of oil) are characteristic of this century. A correlation between their increased appearance and stone decay is not casual, and their role in the decay of monuments seem to be clearer than in the case of other chemical components. In fact these cenospheres contain many aggressive elements and catalysts, and are characterized by an extensive specific surface (ref.30, 31, 32, 33). They become active when wetted by water, forming a very aggressive solution where the wet deposited acidity is noticeably enriched by the dry deposit already existing on the surface. These particles have been found to be an essential component of the black crusts, which are mainly composed of gypsum crystals in which these soot particles are embedded (ref.34, 35). Analysis of black particles and of the deteriorated layers of urban monuments led to the conclusion that not all the gypsum in the crusts on marble monuments is derived from the transformation of the underlying rock, but it is also enucleated by these black particles (see Fig.2). For this reason they remain more readily embedded in the black crust, or attached to non carbonatic surfaces, such as metals, wood or glass, where they form black gypsum crusts.

The main weathering processes are due to the combined action of rainwater and various atmospheric pollutants (particularly carbonaceous particles). In an urban environment the dry deposit on the surface of a monument may be greater than a factor of ten in comparison to pollutants scavenged by rain from the atmosphere, in both the rainout and washout phases. The way in which the monument surface is wetted is very important. The deterioration of carbonatic rocks in urban areas can be roughly classified into three kinds of visibly distinguishable feature patterns: black, white and grey areas. The way liquid water controls both the rate and the morphology of the deterioration crusts formed on the stone as observed in the field, indicates that local rainfall is a critical factor in determining the type of deterioration (see Fig.3; ref.36 to 41. These results are extensively reported with some inaccuracies in ref.42 (pp 145-148) where the source is not cited).

Black crusts, characterized by gypsum crystals and calcite with carbonaceous particles embedded in the crusts (see Fig.4), are formed in zones where the surface of the monument is only wetted by windborne droplets or by percolation at the edges of the descending streams, but where run-off is prevented. Their origin is associated with the capture of carbonaceous particles and sufficient wetting. Under these conditions an aggressive solution forms on the marble (or limestone) surface which is dissolved and progressively transformed into gypsum which crystallizes, in which the carbonaceous as well as the other particles deposited in the meantime are embedded (see Fig.5). Further gypsum crystals are enucleated by the carbonaceous particles, when these are wetted. This structure is very porous, thus favouring retention of water and capture of other particles. Whenever wetted, the active solution forms and the process of deterioration continues, and the crust grows in thickness at the expense of the underlying stone and also due to the enucleation of further gypsum from the particles. For this reason the damage is a function of the time in which the whole crust is completely soaked and releases the aggressive solution, and not of the so called time of wetness.

Similarly, spherical siliceous particles (smooth, spherical and transparent) have been observed in the gypsum patina of monuments of different countries where coal combustion is important in the production of energy e.g. the Cathedral of Brugges, S. Stephan's Cathedral in Vienna and many English monuments in London and Edinborough. The role played by these siliceous particles in weathering processes shows certain analogies with the oil fired carbonaceous particles (e.g. nucleation of gypsum crystals, contribution of suphur, etc.)

For conservation purposes, it is necessary to completely remove these highly aggressive crusts. Special government intervention, such as the special law enacted for Venice in 1973, which prohibited the combustion of oil in Venice, effectively reduced the sulphur dioxide levels and the airborne cenospheres, but the situation of the black crusts on the monuments, remained unchanged so that the deterioration process continued relatively unalterd.

Zones experiencing heavy run-off are subject to partial dissolution, washout and partial recystallization of the underlying rock. This process results in a thinning of the stone and the formation of small authigenic crystals which are white in appearance (white areas; see Fig.6). The thinning depends on both the chemical activity and the dynamic state of the running water, as discussed earlier.

The grey areas do not have characteristics midway between the black and white ones. Their colour is due to the dry deposition occurring in zones which remain dry (see Fig.7), except for condensation. A greater supply of water would trigger the formation of an aggressive solution and transform the grey areas into black ones. The passage of a rivulet of water would eventually form a white bed. Dangerous chemical reactions are prevented by the scarcity of the water supplied to this zone.

DECAY PROCESSES OF MURALS AND FRESCOES BOTH INSIDE AND OUTSIDE

After having discussed the main deterioration processes on the external surface of stone monuments, it seems appropriate also to consider some of the specific problems affecting exceptionally precious mortars: i.e. murals and frescoes. However, as they are often inside, a brief note would suffice in the context of this paper. We will therefore only report a few examples, relative to the thermodynamic theory that we have proposed in order to identify the causes of the deterioration processes. The clarifying case studies made on the Giotto and Michelangelo frescoes and the Leonardo mural have been extensively described in other papers (ref.43 to 48 and 19).

Conservation of murals and frescoes riseses more delicate and complex problems than conservation of stone. In fact, mortar is more porous, so that the wetting-drying cycles are greater and more distructive; it contains a larger quantity of soluble salts and is more exposed to the risk of efflorescence which covers the image. Mortar has thermal characteristics which vary with the moisture content and these are different from those of the underlying wall. This may increase the diurnal variation of the thermo-hygrometric parameters in relation to the inner wall, thus favouring cracking, mechanical weakening and local detachment. Any modification in the colour of a mural or fresco may be regarded as severe damage, whereas the moderate discoloration of stone may be appreciated. For a painted surface the artistic content is contained in a very thin superficial, delicate layer, whereas carved stone can support a greater loss of material before it may be considered 'damaged'. Deposition itself of pollutants and dust is still 'damage' also in absence of chemical reactions, since it obscures the image and exposes it to the risks of necessary cleaning.

Murals and frescoes are exposed to outdoor as well as indoor environments. In the latter case they are usefully protected from direct rainfall and run-off (in general); nevertheless they are exposed to many other environmental factors, probably of secondary importance, but equally dangerous in the long term. The indoor environment, which should be a limited zone with controlled characteristics in accordance with the needs of conservation is, in general, a malefic trap and an ageing chamber on the contrary.

In the painted room the presence of visitors causes high concentrations of dust and many kinds of particles, carbon dioxide and water vapour, but this is not the only problem.

Heating is commonly set according to the needs of visitors and custodians, and not according to the needs of the art work. In addition, for practical or economic reasons it is switched on and off every day, causing a steep rise and a fall in temperature resulting in a contrary cycle of relative humidity. In a previous section we have discussed the dangerous effects caused by these variations: mechanical stress, transport of soluble salts, efflorescence, etc. In internal environments we must consider in addition other processes. On warming the air in the room, a temperature gradient develops close to the walls (see Fig.8). This is conducive to the thermophoretic deposition of small particles on the surface. The thermal gradient induces in the air close to the wall a density gradient, so that the air in contact with the colder surface begins to sink and a descending stream of cooled air licks the walls. Thus inertial deposition of the largest particles occurs on the surface of the wall.

As visitors are a source of moisture, diffusiophoresis occurs due to the mutual diffusion between water vapour and dry air. There is a net drag of the suspended particles in the opposite direction of the diffusing vapour, i.e. towards the centre of the room, due to the greater mass of the dry air molecules. This effect may be locally counteracted by moisture escaping from the wall. If condensation or evaporation occurs, in the proximity of the surface a Stefan flow is generated (the Stefan flow is a hydrodynamic flow which compensates the backward diffusion of dry air so that no net migration of air molecules takes place). This flow is very effective in transporting particles, irrespective of their size, in the direction of the diffusion of the water vapour. The opposed pure diffusive contribution, computed according to the Maxwell equation, is only 20 percent of the Stefan contribution (ref.49).

When the heating system is switched off, or when doors and windows are open for cleaning, the opposite fluxes are eventually originated. Now thermophoresis gently opposes deposition, the density gradient causes an upward flow, but the inertial deposition, which depends only on the absolute value of the air speed, continues its action with new strength.

It is highly recommended that the indoor temperature be maintained as constant as possible to be in equilibrium with the walls. In order to attain this aim walls and air should be gently warmed, possibly with different systems, and without interruption in the course of the day. The suitable temperature should be choosen on the basis of keeping the relative humidity constant, or that only minor and gradual changes occur during the whole year. As the relative humidity is a function of both environmental temperature and specific humidity, in general it may be more convenient to control the environmental temperature rather than the specific humidity, by controlling the heating system by means of a psychrometer and not just by a thermometer alone.

Lighting is also a serious problem: lamps supply heat to the atmosphere forcing convective cells, thus favouring inertial and thermophoretic deposition of particles on the murals or frescoes. In addition, when the lighting is switched-on, the energy emitted (in a wide spectrum from UV to IR) hits the painted surface abruptly, which is then rapidly warmed, causing a noticeable thermal gradient inside the wall. This overheating on the surface is responsible for mechanical stress and forced drying of the outer layer with an outward flux of moisture. The opposite occurs when the lamps are switched-off: the outer layer in contact with colder air cools and shrinks over the still warm wall, readsorbing moisture. These cycles result in microfractures, flaking off of the tempera and deposition of particles. Lamps with an energy spectrum limited to the visible and with gentle increase of emitted energy till the steady state rate is established, are preferable. Haloid lamps give quite satisfactorily results.

The deterioration as well as the deposition processes and their dynamics can be clearly recognized by measuring: the spatial and temporal evolution of the exchange of energy and moisture between the painted surface and the indoor atmosphere; the spatial gradients of the main thermohygrometric parameters and their evolution; and the forced convection and stability of the indoor atmosphere.

As a first example, an increase in the specific humidity close to the surface is an index of evaporation from the wall; if the equivalent temperature (i.e. the temperature that air would have if all the water vapour were condensed out isobarically, with the latent heat released being used to heat the air) is unchanged, it means that the energy required for the latent heat has been supplied by the air and that evaporation occurs on the surface; if the equivalent temperature increases close to the wall, it means that the evaporation occurs inside the wall, which supplies the energy required.

If the mural is hit by radiant energy, its surface warms and relative humidity decreases in its proximity. Under these conditions if the specific humidity remains unchanged, the wall is not subject to evaporation; if the specific humidity increases, the mural suffers from evaporation. The ascent of warm air licking the surface causes inertial and thermophoretic deposition. Evaporation is in opposition to these effects, reducing the total deposition.

In another case, if the specific humidity increases as well as the relative humidity, it means that evaporation occurs inside the wall due to a local rise in temperature and that the vapour escapes through the capillaries (in this case instead of the relative humidity we could use the equivalent temperature).

Again, if the specific humidity decreases in proximity to the surface, it means that condensation occurs and, if the wall temperature is homogeneous and in equilibrium with the air, the relative humidity indicates the size of the pores which are being filled with water. In this case the Stefan flow favours deposition of particles on the wall.

As another example, if the temperature of a damp surface equals the environmental wet bulb temperature, the cause of wetness cannot be condensation since this temperature indicates that the wall is evaporating, and we must search for the true cause, which has a different origin. If condensation occurs, the temperature of the wet surface should be equal to or lower than the environmental dew point, and in this case the process can be stopped by heating the wall.

It is not only useless, but also dangerous, to attempt to stop condensation by insufflating warmed air. In fact condensation on a clean, flat surface, occurs only when the difference between the surface temperature and environmental dew point is negative, and does not depend on the relative humidity of the air in proximity. Condensation on micropores or in presence of soluble salts occurs also with positive differences. A flow of warm air brings about the undesired inertial and thermophoretic depositions and the formation of efflorescence when the heat supplied by the hot flow eventually raises the wall temperature over the dew point.

These few examples show how a process can be influenced as well as the cause. Therefore, it is, in practice, possible to act directly on the cause, not only on the effects, in order to stop the deterioration process. Such intervention would be completely useless when the causes are still active.

CONCLUSIONS

In general, the deterioration process appears to be rather complex and involves both chemical compounds and meteorological variables, and sometimes a biological attack. General relationships involving pollution levels, bulk deposition and damage, valid for all microclimatic conditions are impossible to find, as meteorological factors should not be only considered boundary conditions, but independent variables which can trigger different processes and must be studied from this point of view. Different Commissions and Research Groups have came to this important conclusion independently (ref.50 to 52).

An analysis of the main deterioration processes induced by meteorological factors, has turned up important consequences that should be studied on the basis of the thermodynamics and the exchange of heat and moisture between surface and atmosphere. Not only the microclimate, but also the microphysical processes, that are in general rather complicated and poorly known, should be the object of interdisciplinary research, since they often furnish the necessary key in understanding the deterioration mechanisms.

It appears that the different weathering observed on marble and limestone actually depends on the way the rain wets the monument: from one extreme a complete washout of the surface (white areas), to the other where the surface is wetted and the dry deposit is not removed but activated (black areas).

A particular case is the slightly wetted surface, i.e. when the water is adsorbed and can't form an aggressive solution. In this case the stone appears well conserved (grey areas). This is a clear demonstration that dry deposition in itself may be not a sufficient condition for the deterioration of exposed stonework, unless water is supplied in sufficient quantity to trigger the deterioration processes. In this respect, condensation plays a minor role compared to rainfall.

The deterioration of monuments depends on the aggressivity of the solution which forms on them when they are wetted. Therefore, especially in urban areas where dry deposition dominates, the concentration of hydrogen ions in rainfall may be of secondary importance in comparison with the contribution of the dry deposition. The concentration of the solution which is formed on the monument surface depends on the intensity of rainfall.

In the case of relatively unpolluted towns, where sulphation is not the main cause of the deterioration process, biological deterioration mechanisms are often very important, due to the activity of epilithic and endolithic microflora and microfauna.

Finally, the case of particularly precious mortars, i.e. with murals or frescoes, has been discussed in order to clarify the thermodynamic method proposed for the analysis of experimental campaigns. To take necessary action one should not act only on the effects but also on the causes.

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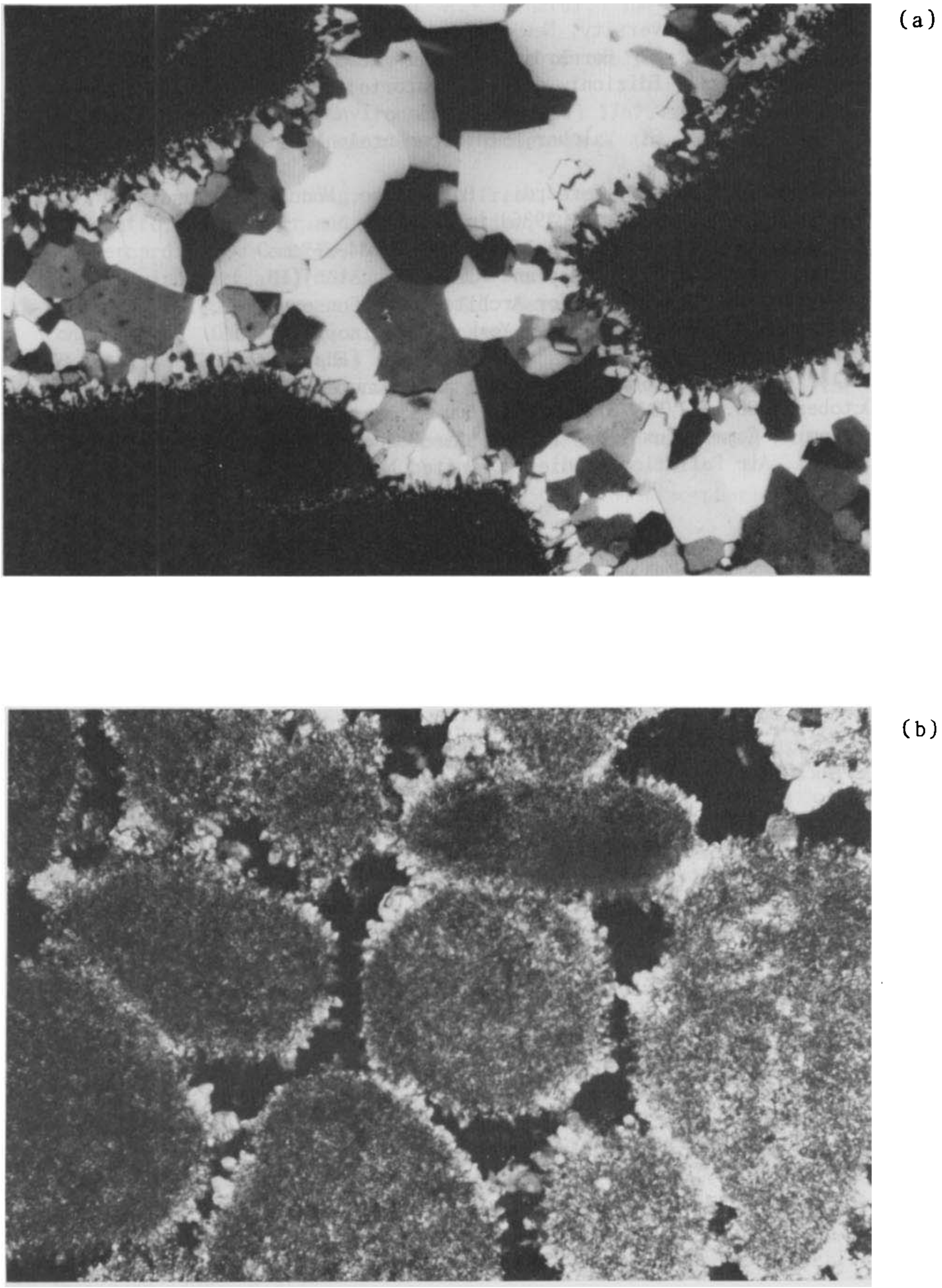

Fig. 1. (a) Gypsum crystallized within the internal cavities of limestone (Nicols X, 465x). (Reduced by 10%)
(b) Oolithic limestone showing calcite crystals reprecipitated on the oolite (Nicols X, 465x). (Reduced by 10%)

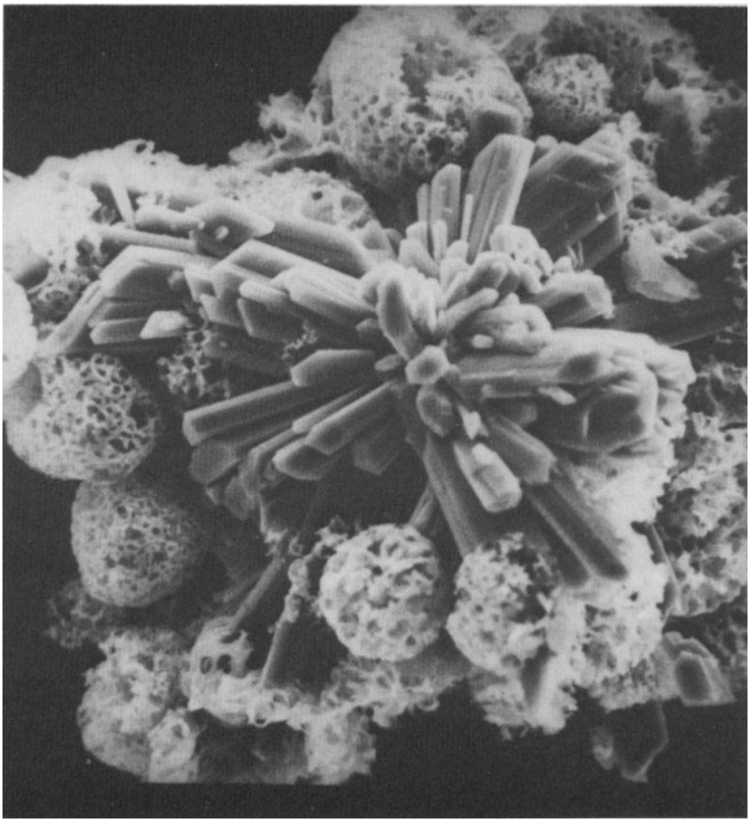

Fig. 2. Carbonaceous particles emitted by combustion processes enucleating gypsum crystals under laboratory controlled conditions (wetting in absence of sulphur dioxide) (scanning electron micrograph, 2500x).

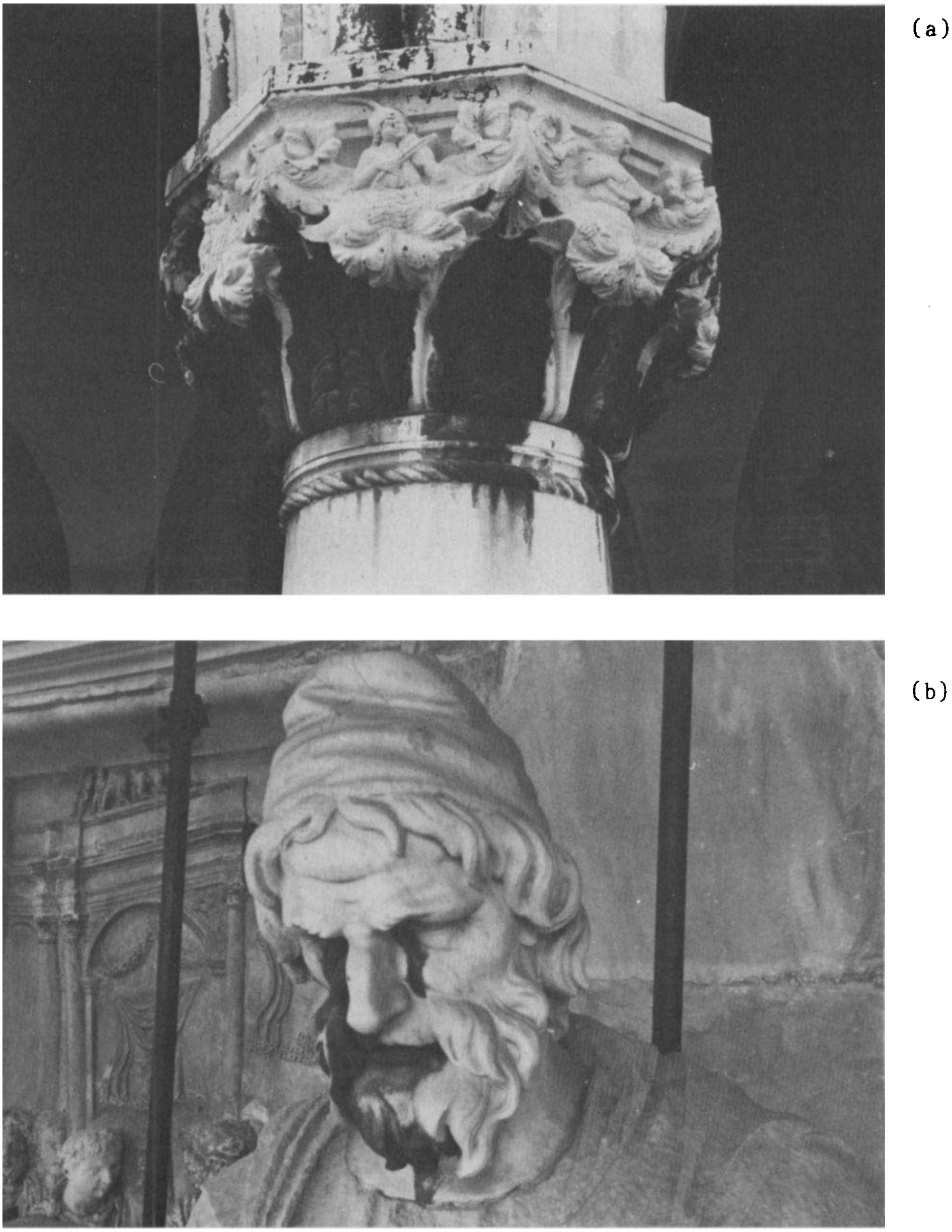

Fig. 3. Examples of white and black areas due respectively to the run-off on the surface (white areas) and deposit of carbonaceous particles and sulphation of the underlying surface in the zones wetted by airborne droplets and percolation, but prevented from run-off (black areas). Their shape is determined by the geometry of the monument. (a) Capital of the Ducal Palace in Venice. (b) Statue on the Constantino's Arch in Rome.

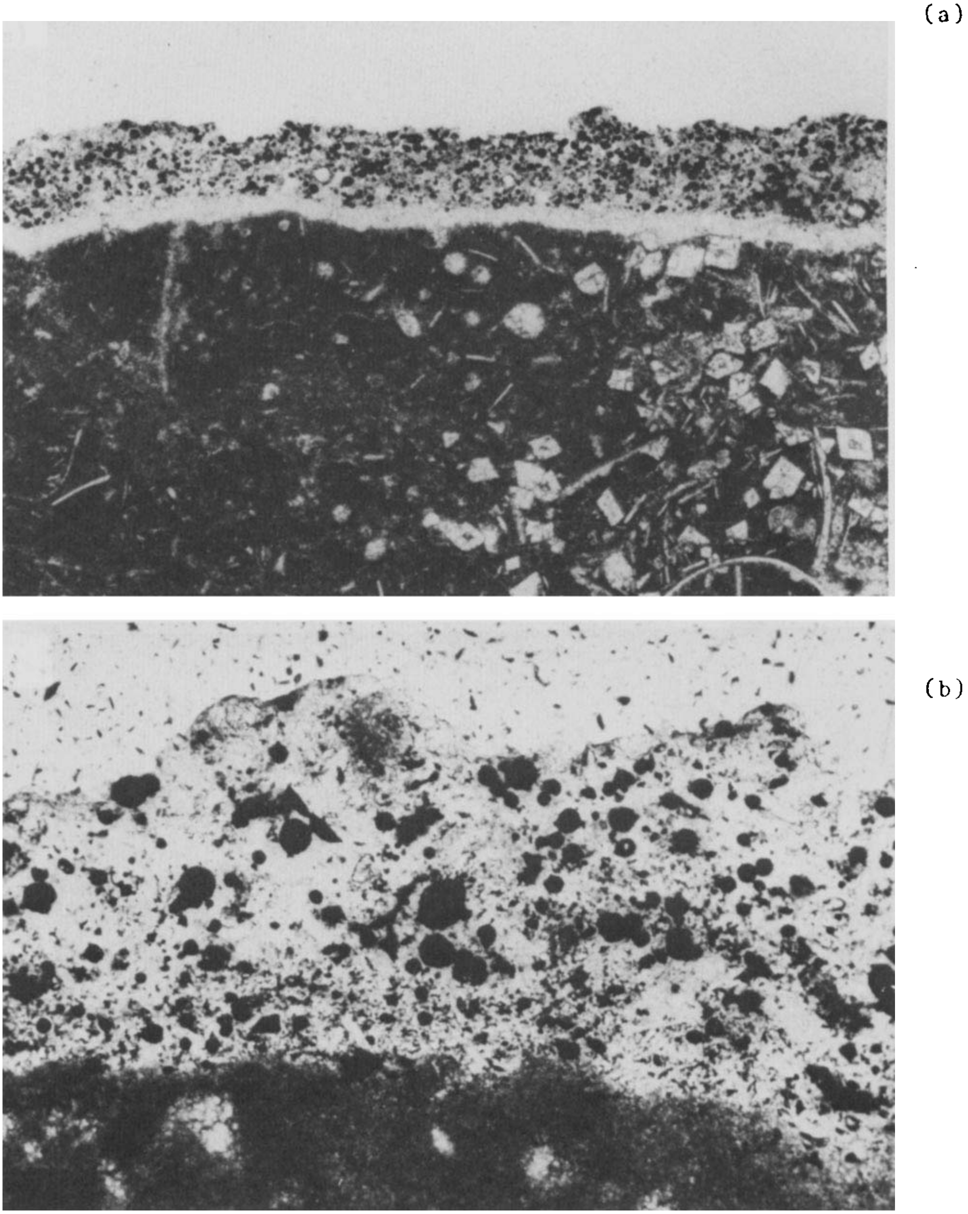

Fig. 4. (a) Black carbonaceous particles embedded in the gypsum crusts are clearly evident. Between the unaltered limestone and the sulphated crust, a layer of reprecipitated calcite (which appears white in the micrograph) can be observed (Nicols //, 185x). (Reduced by 10%)
(b) Carbonaceous particles are uniformly distributed inside the crust (Nicols //, 465x). (Reduced by 10%)

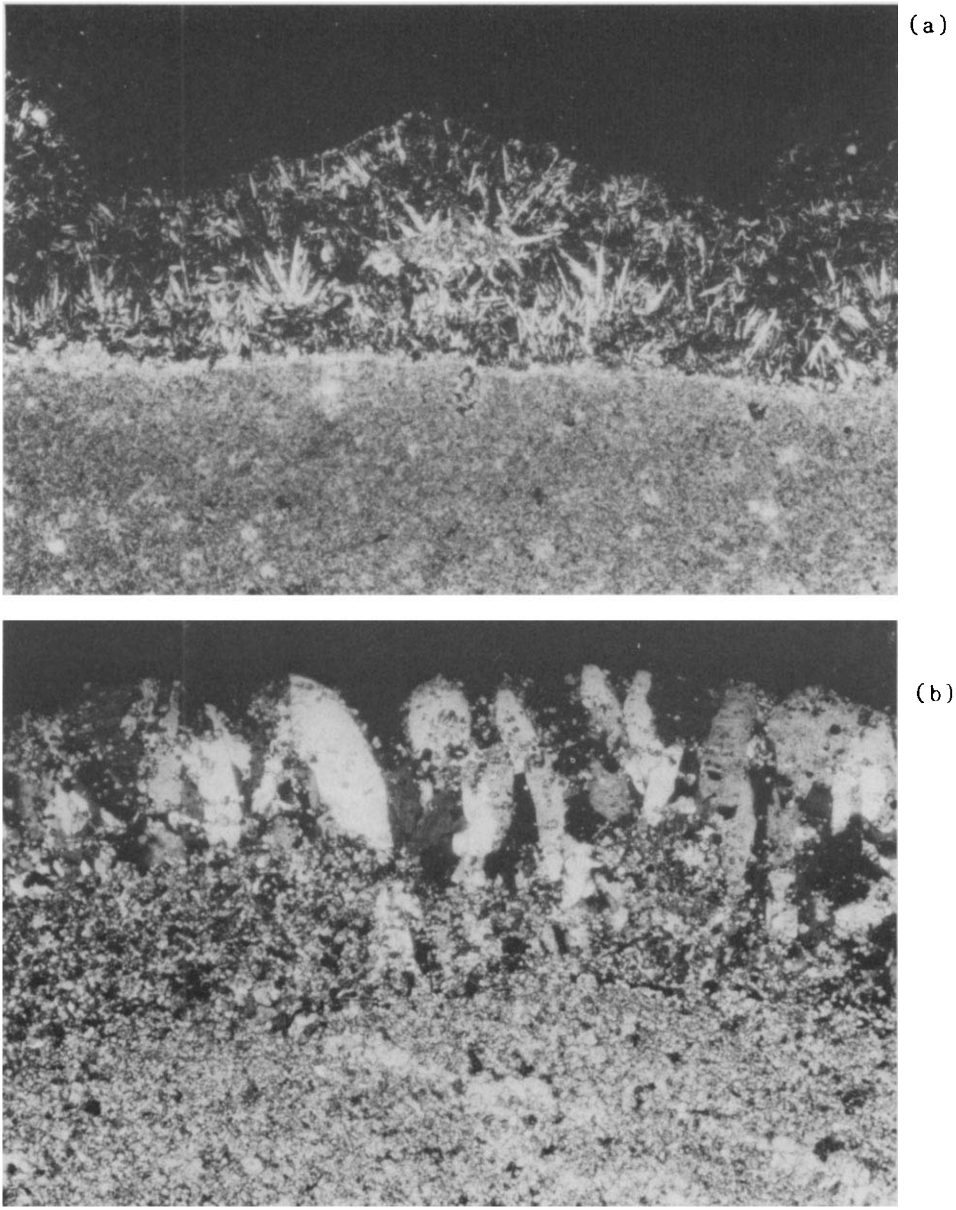

Fig. 5. Examples of a black area observed in transversal thin section.
a) Acicular gypsum crystals with radial orientation grow on the limestone (Nicols X, 185x). (b) In some cases, the sulphated crust consists of authigenic calcite and gypsum (Nicols X, 465x).
(Reduced by 10%)

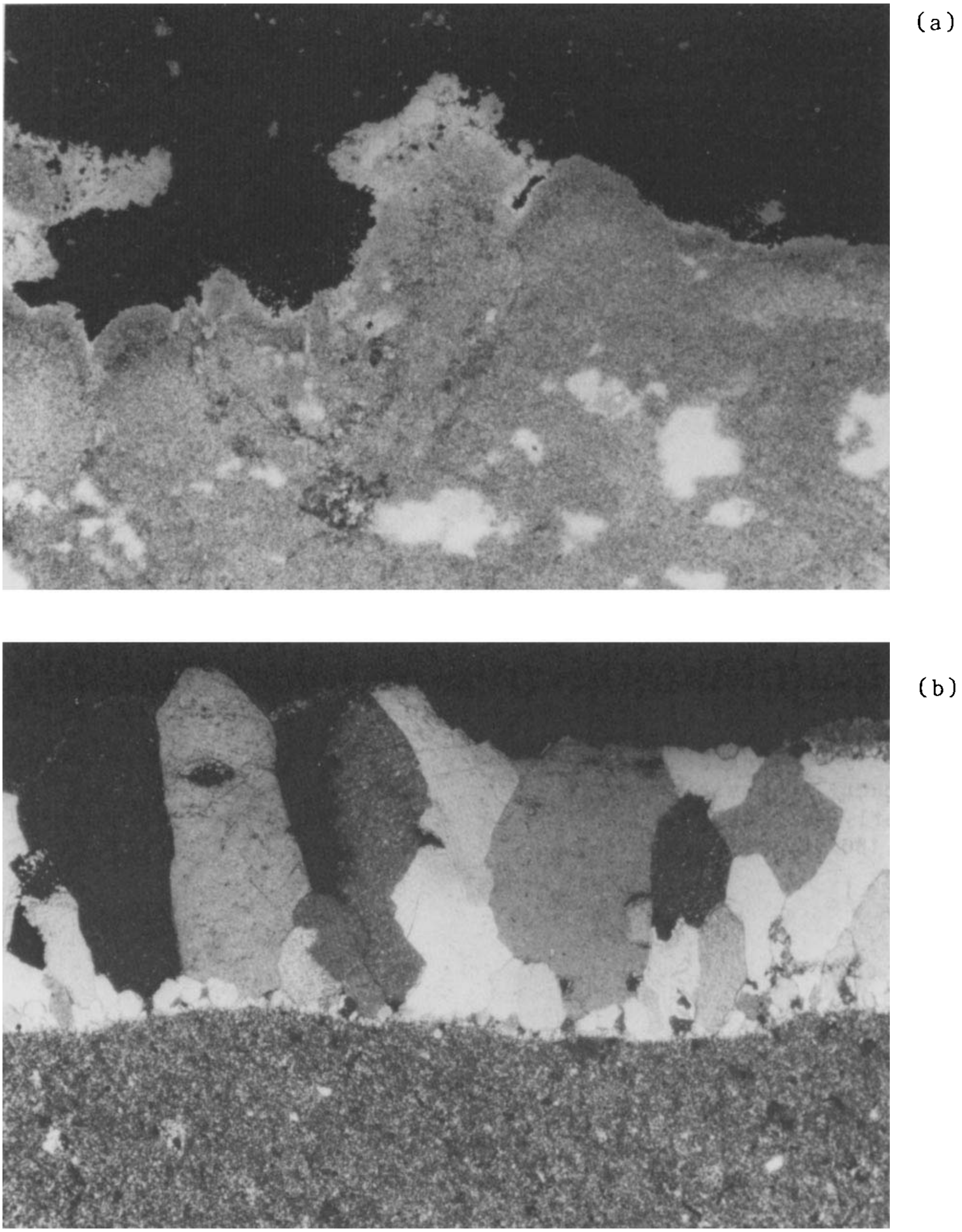

Fig. 6. Examples of a white area observed in transversal thin section.
(a) Dissolution due to run-off produces embayed surface. The washout of unsaturated rain water prevents from reprecipitation (Nicols X, 465x). (b) The reprecipitation of spatic calcite can be observed at the edge of the white area where the run-off is less intense. Generally these white areas show no gypsum (Nicols X, 465x). (Reduced by 10%)

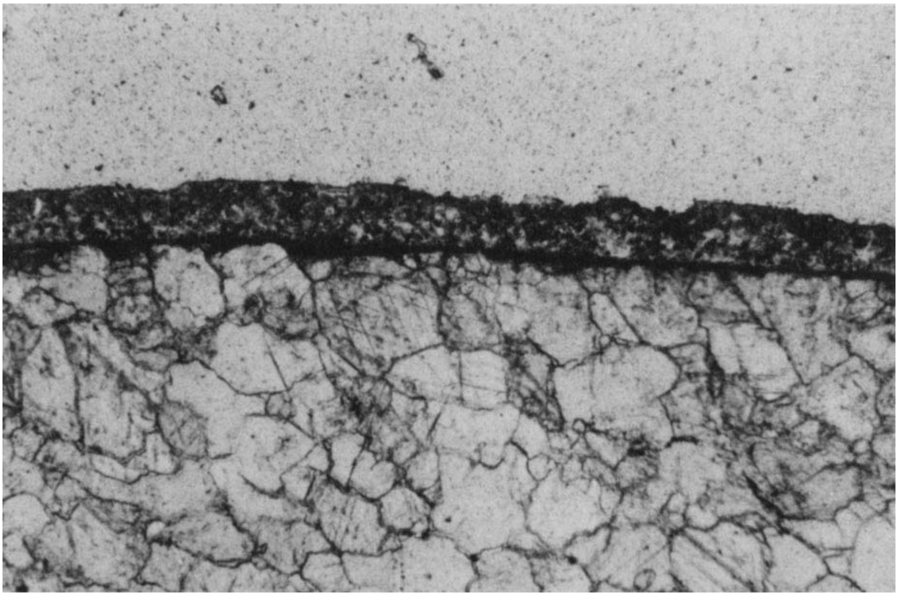

Fig. 7. Transversal thin section of a grey area, showing a compact deposit of particles over the stone surface. The underlying marble appears not to be affected by wethering (Nicols //, 180x).

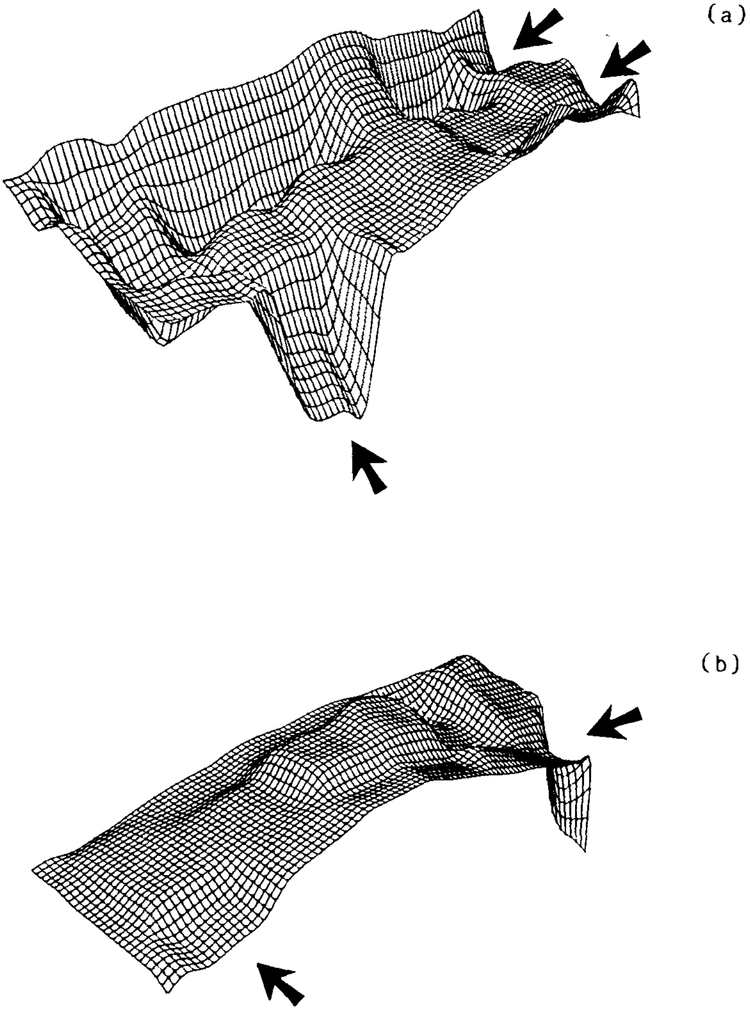

Fig. 8. Thermal maps of the Sistine Chapel, on: 7 May (a), and 9 (b) May 1983.
(a) Situation in the early morning when cold air enters through the open doors (indicated by arrows). The walls are warmer than the atmosphere. Temperature range: 16.8 to 18.9 C (b) Situation at mid-morning when the internal atmosphere has been warmed well above the temperature of the walls. Temperature range: 19.7 to 22.1 C.