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High-resolution microgeophysics: a fascinating challenge. I. Detection of thin patinas

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Abstract - In this paper, the framework of a high-resolution integrated project is presented. Its aims are to attempt to minimize the limits of equivalence and thus decrease those of suppression in the detection by GPR techniques of external growth patinas, intrasample fractures, oxidation surface layers, surface irregularities, etc. Two different sites were investigated (site A and site B) using techniques of crystallography and microgeophysics. Site A shows, with remarkable clarity, over calcarenitic blocks, the transition of the process of patina growth (gypsum and calcium oxalate dihydrate) from areas that are patina-free to those which, instead, are patina-rich. The amplitudes of the waves reflected by the surfaces covered with gypsum and oxalate are sistematically smaller than those from the areas that are patina-free. Furthermore, the waves reflected by the inner planes are characterized by smaller values of amplitudue when the patinas are present and such a decrease peaks in the 1.4 - 2 MHz frequency range. Site B is characterized by large calcarenitic blocks which are considerably more decayed than those of site A. Gypsum is the primary patina constituent. In practice, the site consists of patina-rich (often in the course of detachment) and patina-detached areas, since much gypsum has fallen apart, thus exposing, once again, the calcarenitic substrate. Here, as was the case for site A, the values of the amplitudes are smaller for the areas covered with patina. Such a behavior, however, can vary considerably since it is controlled by the degree of compactness and attachment of the patinas to their substrates. Furthermore, in the areas covered by patina the spectra that are produced by the more internal reflections are distorted and amplified as a result of resonance effects from shallow patina exfoliation phenomena.

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1. Introduction

Over the last two decades the field of Applied Geophysics has been shifting away from its classical targets due to demands for novel applications which originate, primarily, from environmental, engineering and cultural heritage investigations.

Such a task has been facilitated by the rapid development of digital techniques which has fostered novel technical and scientific tools in the theory and practice of data acquisition, processing and interpretation, thus enabling geophysicists to face new fascinating challenges. Frequently, these challenges promote hard questions, particularly in relation to the degree of resolution which is attainable, both in space and time domains, as it is often the case, especially, in engineering and cultural heritage applications.

One such challenge is the possibility of detecting thin layers. These are defined as those whose thickness is a very small fraction of the whole which is being investigated. Depending on the geophysical technique chosen and relative parametric contrast, quantification of such a thickness may vary considerably. In practice, a lower detectablity-limit ranges between 0.01-0.3 of the total. Such a result is regulated by the equivalence principle (which borders with the suppression principle in the case of thin layers) both in potential and wave field techniques.

Detectability decreases with layer thinness and depth within the samples. Typically, only layers which are external to the samples and/or thick enough lend themselves to be detected and assessed using conventional micro- and/or macro-geophysical techniques.

In particular, in wave field tomography the low resolution of thin layers, either in reflection and/or transparency mode, is ascribed to inadequacies in the treatment of the data. Usually, in fact, such an analysis relies solely on a kinematic analysis of the data and this, eventually, verifies only a single physical parameter, namely the wave velocity (or slowness) within the sample, as calculated using travel times. In so doing, travel differences due to a thin layer become, in practice, too small to be detected since they are embedded in the general noise.

Our research focuses on the attempt to minimize the limits of equivalence and, thus, decrease those of suppression using new approaches in the course of project evaluation, data collection, data processing and interpretation. Detection of external growth patinas (i.e. those of gypsum, calcium oxalate, etc.), intrasample fractures, oxidation surface layers, surface irregularities, etc. become thus prime examples of challenges thus far unanswered and that may be successfully modeled using thin layer methodologies.

These methodologies are best studied if the samples involved are monitored using techniques that are capable of providing an appropriate degree of spatial and physico-chemical resolution. Such a demand calls for an integrated research (Cosentino et al., 2002). This was carried out using crystallographic and micro-geophysical studies. To this extent the crystallographic work spans studies of molecular building, x-ray three-dimensional structural analysis, electron microscopy (scanning-transmission) and electron microprobe microanalysis. Concomitantly the geophysical techniques used were electric, electromagnetic and sonic tomography, even though we shall only deal with reflection radar tomography in this particular work.

This work presents some of the general results of this collaboration. A more complete theoretical and experimental report will be discussed elsewhere.

2. External gypsum and calcium-oxalate patinas

Often films (patinas) of different materials grow upon the different substrates that constitute the external surface of commercial and historical artifacts (monuments, buildings, etc.). These films may grow in various shapes and forms according to different growth kinetics, this kind of process is intimately related to a number of physical (i. e. type of substrate) and local parameters (i. e. availability of sulphates, acid rain, urban pollution, specialized exposure, etc.). Especially in urban environments, certain microenvironmental conditions may, over time, foster the juxtaposition of different patinas upon a common substrate.

The patina-growth process usually commences by the interaction with certain anionic groups of a key cation in the substrate. This leads to the formation of inorganic and/or organic salts. The process may involve just a few molecular layers of the substrate or, eventually, proceed to the point of compromising its overall cohesion and stability. In addition, the very process of patina formation can become so crystallographically disordered as to result in thick, poorly bonded patinas. Over time, these patinas may become prone to breaking apart and/or even detaching themselves from their substrates.

Patinas may initially extend as a very thin film (a few micrometers) of varying color which covers the entire substrate surface; in so doing they can eventually act as a novel template for another different patina (i.e. the juxtaposition of gypsum over a calcium oxalate film). Otherwise the patinas may grow in the form of patches randomly scattered over the substrate surface. Careful examination suggests that such growth independence is often only apparent since localized patina growth is usually catalized by specialized local occurrences.

Patinas may range from a few angstroms to a few centimeters in thickness. Usually they become embedded during growth with other material (silicates, carbonates, pollution material, trace elements, etc.) that is characteristic of the particular micro-environment where growth takes place.

Since their growth may result in serious aestetical damage and, above all, loss of substrate surface, patinas must be properly located and diagnosed prior to planning any restoration effort. To this extent positive characterization of substrate and patina sample material is usually carried out via a number of tests of increasing analytical sophistication (optical and polarized microscopy, electron microscopy (scanning-transmission), x-ray microanalysis, x-ray diffraction, etc.).

Patinas may grow on just any surface. In this work we shall focus on the detection of calcium oxalate and gypsum patinas since both routinely grow on stone artifacts (monuments, buildings, statuary, etc.).

Calcium oxalate patinas are primarily composed of calcium oxalate monohydrate (*COM* or whewellite: $CaC_2O_4 \cdot H_2O$) and calcium oxalate dihydrate [*COD*: weddellite: $CaC_2O_4 \cdot (2 + x)\, H_2O$]. Typically, the patinas are either *COM* or *COD* or a mixture of the two. Occasionally, some calcium oxalate trihydrate [*COT*: $CaC_2O_4 \cdot (3 + x)\, H_2O$] is found in association with *COM* and *COD*. This is a very rare occurrence since *COT* stability is critically dependent on acidity conditions (Deganello, 1986).

Thermodynamically *COM* is the most stable phase; in due course, however, *COD* undergoes a phase transition to *COM* under suitable temperature and, above all, humidity conditions.

Gypsum patinas have gypsum as their primary constituents. They may grow as primary material over a substrate or, as is often the case, juxtapose upon calcium oxalate films. These provide the ideal template for gypsum growth. Such calcium oxalate templates may have different thicknesses; at times they may be as thin as 2-3 μm. There is only one independent calcium site in gypsum ($CaSO_4 \cdot 2\ H_2O$) and that is coordinated by eight oxygen atoms. Six of those belong to four adjacent sulphate groups while the remaining two belong to water molecules. Sulphur coordinates four oxygen atoms; all of this results in layers comprising calcium, sulphate and oxygen atoms parallel to the (100) planes (Fig. 1). These planes, which are linked to one another through water molecules, turn out to be very important in the damping of electromagnetic waves, depending on the direction of wave arrival.

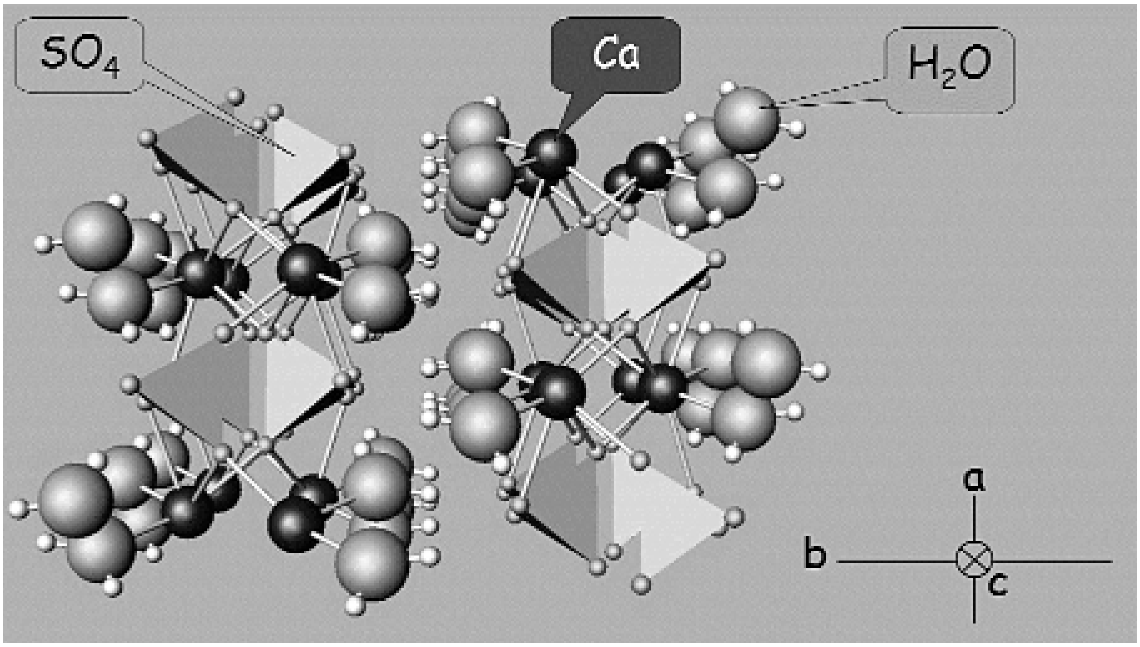


Fig. 1 - Selected view of the crystal structure of gypsum with reference to crystal axes.

All of the above patinas share calcium as the critical oxygen-coordinating cation. This calcium atom usually gets to the patinas through the substrate, typically a calcareous one. The net result is a chemical and structural impoverishment of the latter as the patinas grow.

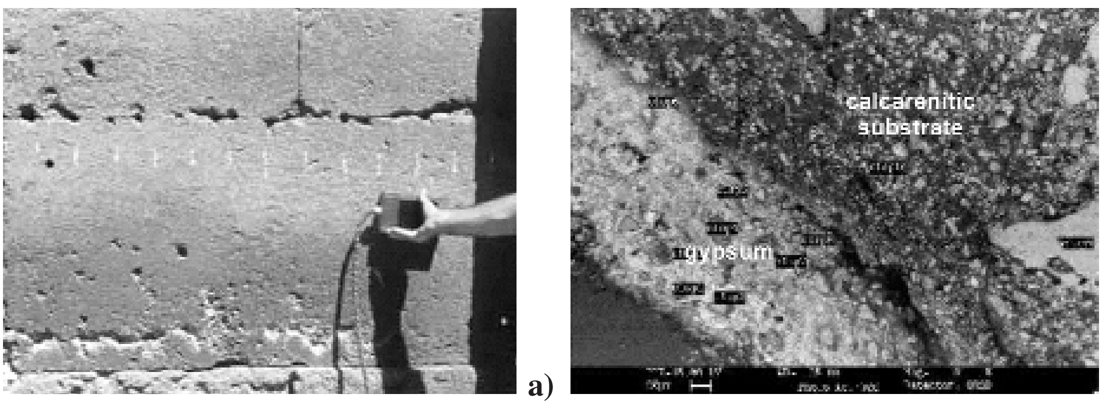
Since *COM, COD* and gypsum present themselves as distinct layering sequences at their interfaces with their carbonatic substrates, it became clear that the individual atomic structures of each structure type ought to specifically affect the spectral characteristics of the traveling electromagnetic waves. The physical properties of a material are, in fact, always controlled by its atomic-molecular organization. The various individual atomic species and sizes, as well as their interatomic distances and voids within each crystallographic plane become thus preferential discriminators of individual structural properties. These are anisotropic; consequently, only if the process of patina growth were to routinely take place along the same planes could one confidently expect similar interaction values with the electromagnetic waves along that specific growth direction. In practice this is not the case. As patina growth proceeds away from the carbonatic interface, it tends to become more spatially irregular. Consequently, we expect that the spectral interaction of the various crystal planes with the magnetic and electric field be, in effect, averaged but still diagnostic enough. Such relationship between crystal structures and physical properties has been tested and will be discussed in forthcoming papers.

3. GPR experiments carried out in different sites

Two different sites, characterized by large carbonatic stones and various degrees of patina growth were investigated in the city of Palermo using semi-transmission conditions. This methodology consists in the positioning of the radar antenna on the surface of the artifact (with or without patina) in order to receive different sets of reflected waves. The first such set is reflected by the most external surface layer (this being a patina - if the latter were to be present - or, otherwise, the carbonatic surface). Such wave set corresponds to the first wave arrival which is recorded on the signal trace. The following wave sets are, instead, reflected by potential intrastone planes that discriminate local variations in wave velocities. Should no intrastone plane be present, there will be, however, at least one reflecting plane: this coincides with the innermost surface of the wall.

The waves so reflected arrive a few nanoseconds after the first wave set (Fig. 2b). Such a delay depends, to a large extent, on the depth in the stone of the first reflection plane whose precise location, in practice, is unknown. As a consequence an additional variable is introduced in the process of data interpretation and this, in principle, may jeopardize potential comparisons.

The semi-transmission approach is bound to work only when the travel of the electromagnetic waves through the patina layers significantly influences the dynamic characteristics of the crossing waves, resulting in resonance (or absorption) phenomena that



a) b)

Fig. 2 - Patinas at the Ucciardone wall: a) patina is much more noticeable in the lower half of the block. Notice transition of the process of patina growth. b) SEM microphotograph of patina. This primarily comprehends gypsum and, subordinately, calcium oxalate dihydrate. Black marks refer to EDS analysis here not reported. Notice the interface between the calcarenitic substrate and gypsum.

selectively amplify (or damp) particular values in the radar frequency range.

We used three high-frequency antennas, whose bands are, respectively, centered on 1000, 1500 and 1600 MHz. The bands of the incoming waves vary slightly from antenna to antenna, but, near their transmitting dipoles at least, broadly range between a few hundred and 2500 MHz. Lower frequency antennas are made by GSSI (USA) and the higher frequency one is made in Italy (IDS, Pisa).

The first experiments were carried out in three areas of the outside walls of the Ucciardone building in Palermo (site A; Cosentino et al., 2001). This site was chosen after a very extensive search since it showed, with remarkable clarity, the transition of the process of growth of, predominantly, gypsum and calcium oxalate dihydrate patinas from those areas which were, instead, patina free. Such patina-free and patina-rich (up to 200 m, see Fig. 2a) areas were present in single stones measuring about 1 m along one direction and this allowed us to scan them by GPR along the same stone blocks. Such size requirement is of fundamental importance in this initial analysis of GPR response. Only on large stones, in fact, are we able to acquire a sufficient number of signals that can be reliably stacked so to remove noise in both time and space domains. On smaller surfaces, instead, stacking suffers considerably more from the potential noise introduced by variations in patina thickness and cohesion, patina bonding as well as structural and morphological defects of the walls.

The acquisition parameters, using a 1500 MHz antenna, were 16 bit for sampling, 1024 samples for scanning and 32 scans per second, with a scanning velocity of about 2 cm/s.

Each profile was acquired ten times and showed excellent reproducibility within the limits of the experimental errors. A typical profile crossing the separation between patina-rich and patina-free areas is presented in Fig. 3.

Furthermore, prior to analyzing the spectral characteristics of the various wave arrivals,

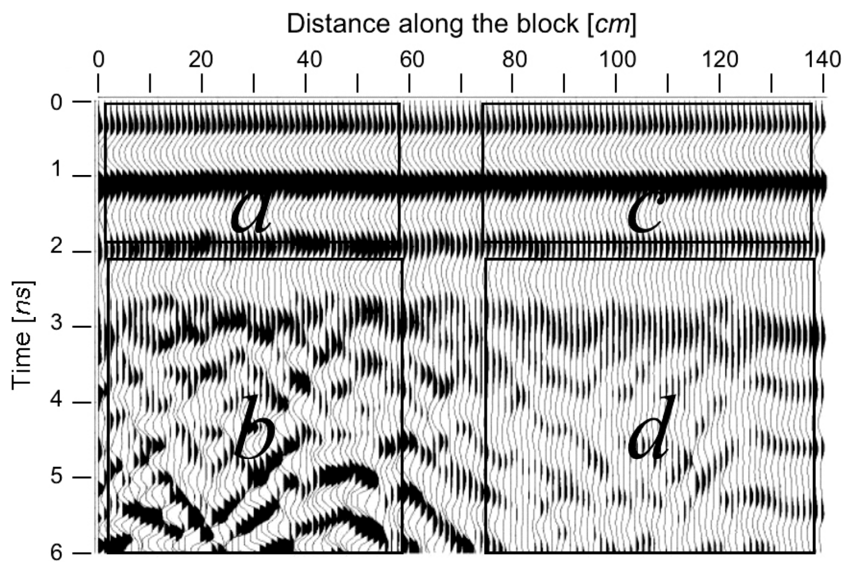


Fig. 3 - Typical file recorded in site A. The profile crosses the separation between patina-free and patina-rich areas at about 65 cm. The spectral responses of the parts of signals contained in frames *a*, *b*, *c* and *d* are, respectively, presented in Fig. 5.

we imposed a stacking procedure of over 1 s (about 2 cm of scanning along the profiles) in order to build a data set of high stability. The signals were then evaluated and the sections comprehending the reflections from the most external surface (first signal arrivals) were analyzed separately from those producing the reflections from inside the stone walls. The discriminating time was estimated at about 2 ns (see Fig. 4). This value is expected to mark the boundary between the signals from the most external surface (which are very stable since the two-way time travel is in the air) and those traveling within the sample. It should be, however, stressed that such an evaluation is quite subjective, and may be prone to potential adjustments from site to site, depending on the depth of the shallower reflection and the permittivity of the sample.

The results are particularly interesting. One first notices that the amplitudes of the waves

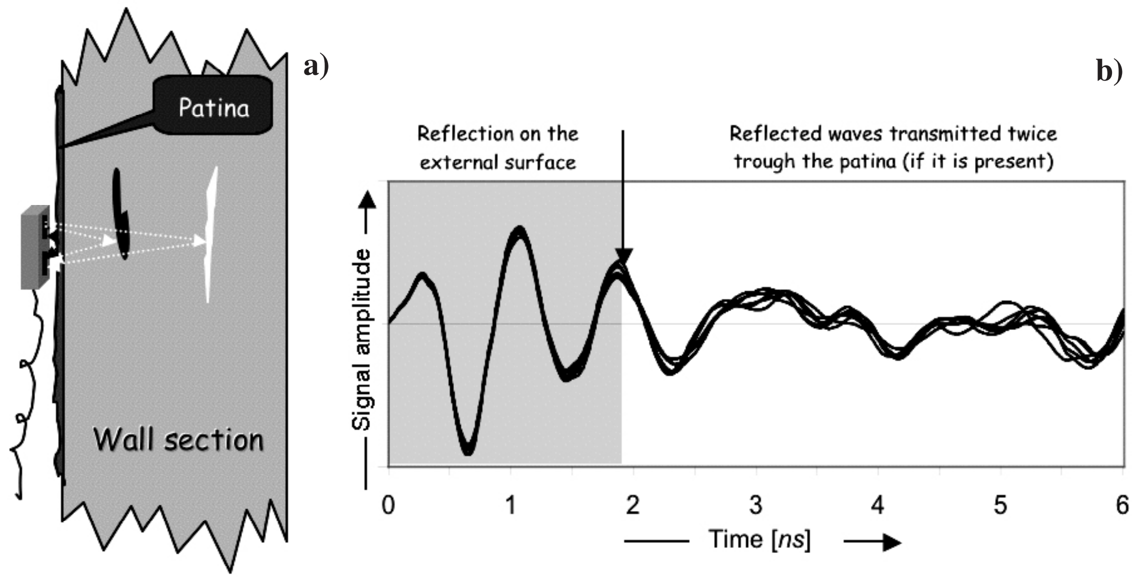


Fig. 4 - a) Sketch of typical GPR acquisition along the surface of the wall using semi-transmission techniques. b) Traces of GPR signals (site A) showing the shape of first arrivals (gray zone) and that of later arrivals (about 2 ns delay). These, in presence of an external patina, cross twice the patina layer.

reflected by the most external surface of the wall are systematically smaller if the latter is covered by an alteration patina, even though the general characteristics of the spectra are similar to those produced when the external surface is patina-free. This effect may be due to a lower reflectivity on the part of the patina layers. Furthermore, and most importantly, the waves reflected by the inner planes not only are characterized by overall smaller values of amplitude when the patina is present but, in addition, show that such an amplitude decreases peaks in the frequency range 1.3 - 2 GHz (Fig. 5d).

This notwithstanding, the results need statistical confirmation in order to be generalized. Consequently, we commenced to test sites characterized by patina occurrences somewhat similar to those encountered in the walls of site A. Three different occurrences were located on the walls of Vittorio Emanuele street, between Piazza Marina and the so called “Passeggiata

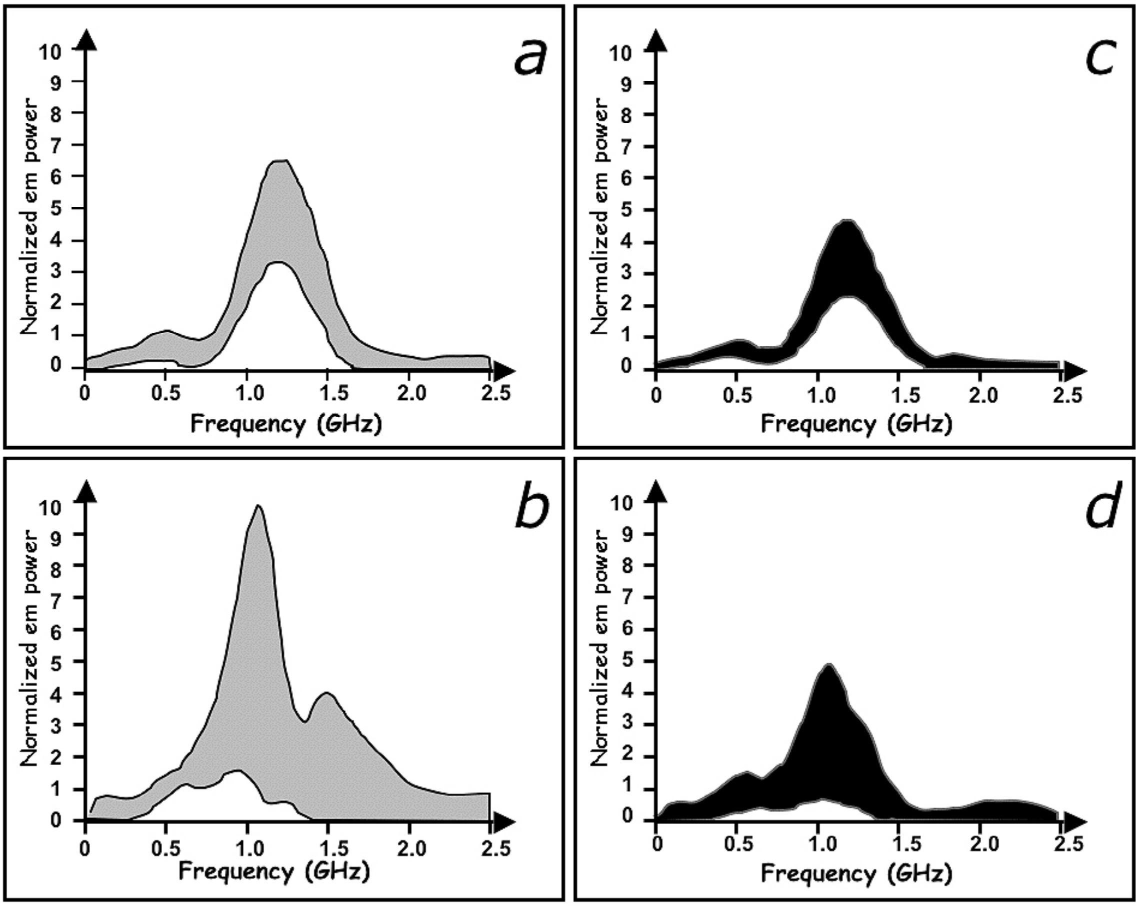


Fig. 5 - Spectral responses of parts of signals presented in Fig. 3. Spectra *a* and *b* refer to patina-free areas while *c* and *d* to patina-rich areas. Notice damping of amplitude in *d*, especially in the 1.3 - 2.0 GHz frequency range.

delle cattive", in Palermo (site B).

This site B is subject to high urban pollution. Its walls are made of large calcarentic blocks as are those of the site A; there is, in addition, widespread occurrence of patina growth and this is, primarily, gypsum. Here, however, the overall process of stone decay is considerably more advanced than at site A. The gypsum patinas are, on average, considerably thicker (up to about 500 μm) and more poorly attached to their calcarenitic substrate with the result that, often, they have fallen together with part of the substrate, thus exposing once again a calcarenitic surface. These newly exposed surfaces, however, tend to be quite coarse and embedded with traces of the patinas that juxtaposed on them. Contrary to the situation studied at the site A, where the patina-free and patina-rich areas were very clearly ascertained, here it appears more realistic to describe the sites as consisting of patina-rich (often in the course of detaching) and patina-detached areas.

The acquisition parameters, using a 1600 MHz antenna, were 16 bit for sampling, 2048 samples for scanning and 16 scans per second, with a scanning velocity of about 2 cm/s.

The profiles so recorded are quite different from those of site A. In particular, the two-way travel times of the waves reflected inside the wall appear to be shorter and this prompted us to evaluate them at about 0.8 – 1 ns (Fig. 6). This would position the origin of such reflections at a depth of a few centimeters within the stone. These reflections are most likely caused by the presence of water which penetrates the stones through a soil terrace located on the backside of the walls.

The spectral analysis, carried out in otherwise identical fashion to that of site A, shows that

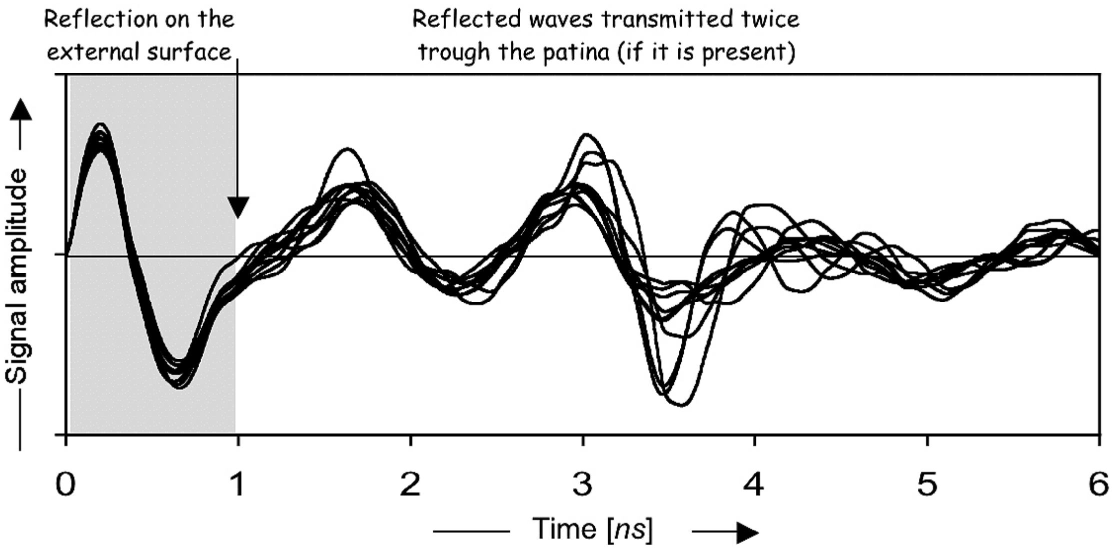


Fig. 6 - Typical signals recorded at site B. Notice that the two-way travel time of the waves reflected inside the wall appears to be shorter than in fig. 4b. This delay, on average, is estimated at about 0.8 - 1 ns.

the values of the amplitudes of the first arrivals (outermost external surface) tend to be smaller for the areas covered by patina, as was the case at site A. Depending, however, on the degree of compactness and attachment of the patinas to the walls, such amplitude values tend to vary and, even, invert with the result that in a particular instance the areas with patina show even higher reflecting power.

In addition, the spectra that are due to more internal reflections are, instead, distorted and amplified in the areas covered by patina. These areas evidence resonance effects which vary from sample to sample along the entire 1-2.5 GHz range.

The above behavior is rationalized by the very nature of the surfaces. These are particularly irregular where the process of patina detachment is completed. Such a detachment results in partial exfoliation of the original surface of the calcarenitic substrate (Fig. 7). Since the resulting degree of coarsness is of the order of a few centimeters and, thus, commensurable to the wavelength used, surface scattering results in reduction of the amplitude of the reflected waves. This would explain the similarity in reflectivity measured for patina-rich and patina-free areas. In addition, as earlier anticipated, the patina-rich areas are, often, layers of juxtaposed material (gypsum over gypsum and air over gypsum) which tends to produce multiple reflections (resonance) at particular frequencies, depending on the thickness, separation and nature of the

Fig. 7 - Example of process of advanced patina exfoliation at site B. Here the patina is composed mainly of gypsum.

various strata of materials involved. All of this can be correlated to a considerable extent with the properties of the crystal structure and morphological layering of gypsum (Fig. 1), as will be discussed elsewhere.

4. Conclusions

Because of the regular transition of the decay process between patina-free and patina-rich areas and, even, the relatively modest extent of the very decay process, the Ucciardone building presents an almost ideal testing opportunity. It does not surprise, thus, that the results obtained were particularly impressive and easy to correlate with crystallographic observations. They, however, cannot and should not be generalized to other occurrences, yet. We need much more integrated work on other patina models in order to collect meaningful data sets covering different situations. Only then will it be possible to assess the very limits of our studies.

Such remarks are well evidenced by the work on the walls of site B. Here the data, although self-consistent and readily relatable to those of Ucciardone's, nevertheless stress the degree of variability which is involved in the processes of patina growth and the consequences that such a variability may bring to GPR work.

It is, nevertheless particularly refreshing to notice that, within the limitations of the

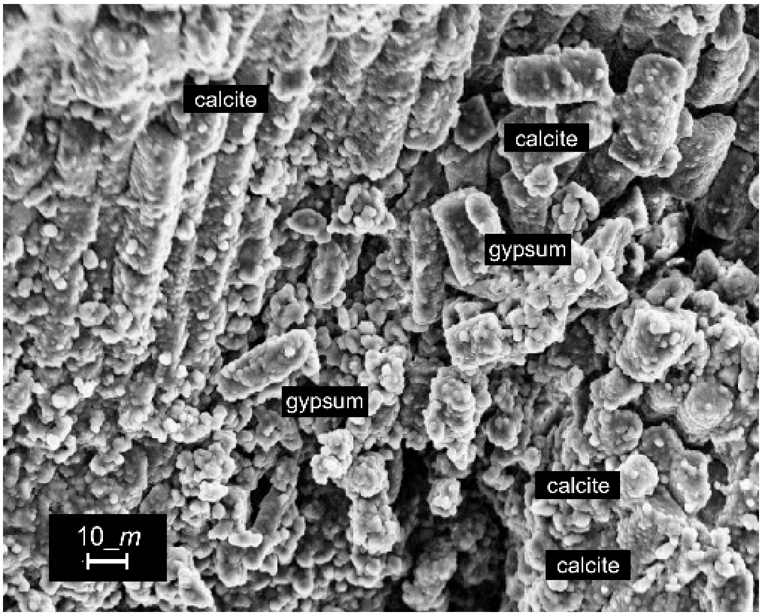


Fig. 8 - SEM microphotograph of a patina in site B. Notice loss of cohesion of calcite and overall growth of gypsum. Reflection on the external surface.

wavelength used, the GPR techniques are capable of detecting the effects of at least some of those processes of growth once the dynamic characteristics of the signals are analyzed. Clearly, and this should be stressed, such an analysis is no longer possible if the kinematic aspects only of the signals are considered.

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