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Original article

Ancient materials specificities for their synchrotron examination and insights into their epistemological implications

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ABSTRACT

The synchrotron characterisation of archaeological and heritage materials has undergone a steep development in the past years, among a range of other advanced characterisation techniques. For synchrotron techniques alone, close to a hundred articles were published in 2011 on such materials, prompting new developments at large scale facilities. However, few publications have discussed the specific characteristics of heritage materials in their advanced spectroscopic and imaging study. Here, we suggest that a greater consideration be put on the specificities of ancient materials and their theoretical implications on the analytical process. In particular, we discuss the importance of the *a posteriori* framework of the study of *heterogeneous* materials considered in their *historicity* as structuring parameters of their study. Major implications are the relevance of trace analyses, those of majors and we suggest, more importantly, the dynamics between both endpoints. The on-going development of multimodal spectral imaging appears as a way to better address corresponding difficulties. Epistemologically, we suggest that a reflexive approach be developed to explain, structure and possibly contribute to narrowing down the field of possible methodological research.

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1. Research aims

The characterisation of Cultural heritage materials raises many new and crucial questions in terms of methodology. However, few publications have discussed the specific characteristics of these materials in their advanced spectroscopic and imaging study. Here, the results of our investigation are based on the methodologies, particularly based on synchrotron techniques, that were developed to study heritage samples at microscale. Our research aims are to develop a reflexive approach, which involves specifying the language that describes the scientific operations performed when studying heritage artefacts using advanced spectroscopic and imaging means, and proposing an epistemological framework of reference for such a reflexive analysis. Methodological research on our complex systems may therefore benefit from this new approach, and thus main directions taken in corresponding developments be refined and more soundly justified.

2. Introduction

In addition to stylistics, geochronological information and historical sources when available, the microanalysis of materials from archaeological contexts and objects of cultural heritage leads to essential information for the associated fields of research [1–4]. Several main academic divisions are encountered in the field, primarily these of the Humanities where archaeological artefacts are primarily seen through the prism of Human cultural behaviour, of Environmental sciences and of Material sciences (Physics, Chemistry). In their *cultural* meaning, ancient materials are primarily envisaged as source of knowledge for human/social science, related to academic fields such as Archaeology, Art History, History of Sciences and Techniques. Here, main issues at stake relate to the provenance of raw materials and the distribution of artefacts and goods, to operating sequences (past manufacturing techniques, technical art history, use of artefacts, consumption), to populations (nutrition, pathologies, death, *etc.*), to the identification of objects (attribution, chronology), to mediation (museumology), *etc.* In their *environmental* meaning, research may shed light on occupation sites' palaeo-environments (past climate, landscape), on the influence of Man on its milieu (anthropisation, palaeo-pollutions, combustions), on taphonomy at the site (corrosion, diagenesis), on alteration in the museum environment and of the built heritage (stabilisation, consolidation, restoration, preventive conservation).

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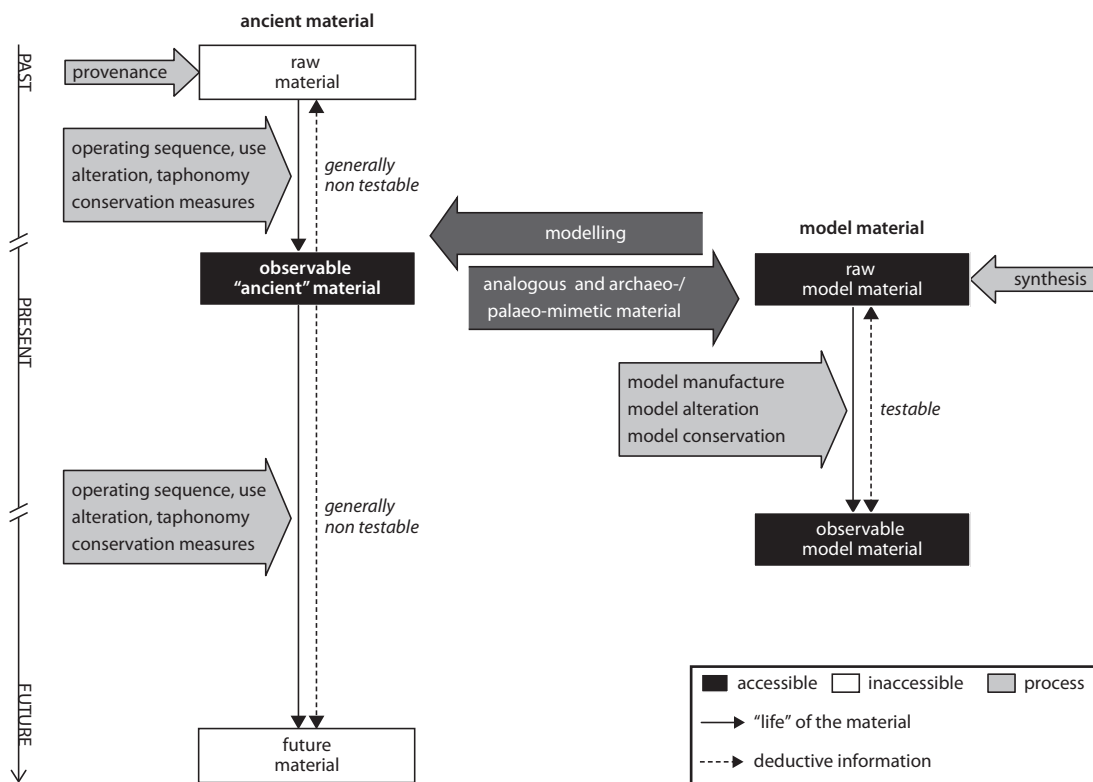


Fig. 1. Scheme showing the flux of information inferred from presently observable ancient materials to gain understanding on their past and future states. To some extent, model materials can be comparatively studied. Analysing ancient materials (as *analogues*) may contribute to predicting the long-term behaviour of modern materials. Information on ancient materials can also tentatively be used to synthesise novel *archaeo-* or *palaeo-mimetic* materials.

However, these divisions are mainly distinctions inherited from the history of scientific disciplines, sometimes reinforced by institutional configurations (such as the distinction within the French CNRS between environmental science at INEE and the Humanities at INSHS). These divisions must be taken into account, but not essentialised as if they reflected real ontological differences: they would conceal the real unity of the field, resulting from the methods used, the nature of the investigations and of the objects under study. Materials at stake are very diverse in terms of their composition, their structure, their morphology as well as their properties. Yet, they bear in common a number of characteristics which strongly influence their analysis. A key feature is their study along scientific procedures optimised to acquire historical information, whether to specify the origin of an artefact, its use, its alteration, *etc.* They are therefore part of a larger set of materials which are studied from the viewpoint of their *historicity*, that we have proposed to designate as *ancient materials*. The term “ancient materials” will be employed throughout this paper and preferred in this context to others such as “archaeomaterials”, “(cultural) heritage materials” or “archaeological materials”.

Ancient materials are also a source of inspiration for material sciences (chemical and physical behaviour including during short and long term ageing, novel materials and processes, methodological approaches: instrumentation, data processing). Their study may allow incorporating some *archaeo-/palaeo-mimetic* properties into modern materials. For instance, ancient materials often present exceptional properties, particularly in terms of durability (resistance to weathering, to fading, *etc.*) and elaborated optical appearance (color). The reemploy of past, and sometimes “forgotten”, manufacturing techniques may also lead to new routes of chemical synthesis and to new materials (Fig. 1).

An example is the study of archaeological lead-based cosmetic recipes that fostered ideas on the soft chemical synthesis of galena (PbS) nanocrystals in an organic template [5,6]. This may be seen

as a complementary concept to the use of archaeological systems as *analogues* to predict the long-term behaviour of existing materials, such as that of glass or metal vessels used in the storage of radioactive wastes [7,8].

The study of such complex systems may involve many instrumental approaches from portable instrumentation, benchtop devices to large-scale facilities. In particular, the past ten years led to a quasi exponential increase in the results published on ancient materials using synchrotron techniques with more than 600 publications known to the authors in the 1986–2011 period (including palaeontology and palaeo-environments) [9–13]. The fact that 50% of these publications are less than 5 year old illustrates the fast rise of the use of synchrotron techniques for the field, in phase with the general increase of reports of the use of synchrotron. In the near future, synchrotron techniques could be considered as a routine tool for the field complementing more accessible portable and laboratory-based instrumentation.

The synchrotron microanalysis of ancient materials may provide the identification of chemical compounds, the quantification of physico-chemical or mechanical properties, and improve the segmentation, classification and comparison of the collected data [13–17]. These novel methods of investigation lead to a range of analytical and methodological questions. We here propose this intersection as a manageable framework in which first epistemological considerations are discussed. Our observations clearly extend in part to adjacent fields of material research, in particular in environmental, Earth and some fields of life, forensics and Universe sciences, and to other tools than the synchrotron. A limited number of articles discuss epistemological implications of the specificities of ancient materials on their analysis using synchrotron spectroscopy and imaging [2,11,13–15,18,19]. It is the matter of frequent introductory or conclusive comments in conferences, seminars, academic courses and appears frequently in the grey literature and day-to-day discussions. Main aspects are

exposed by G. Spoto et al. who underline that “the complex nature of the objects studied has often required the use of multi-technique analytical approaches and the application of the entire analytical potential of spatially-resolved techniques”, and that “the ability to spatially resolve analytical information has been a significant breakthrough in the study of remnants of our past” [2].

We suggest approaching these issues from two perspectives. On the one hand, they refer to a thought from history and the sociology of science, based on the corpus of works using synchrotron methods to study ancient materials for the past twenty years, which could tackle the objective to show the gradual construction of scientific practices and analytical frameworks. We hope in the near future to engage in such a diachronic study. In addition, they lead to a synchronic reflection on the current state of synchrotron methods applied to ancient materials from an epistemological perspective. The clarification of theoretical concepts to which this article is primarily devoted has here a dual aim:

- to specify the language employed in the analytical process with very concrete experimental impacts. Without going so far as to say that scientists have the epistemology and the methodology of their research instruments, there is at least a subject for wondering how the use of new technologies affects the experimental work and underlying concepts, and how these can be refined in light of these new techniques²;
- to delineate the intellectual framework of reference within which such scientific research takes place – against a positivistic approach that would only see the use of synchrotron as a way to gain punctual information used in a second phase by historical sciences, restoration or conservation, our idea is that the link between hard and historical sciences is much more complex and closer.

The study of ancient materials is precisely the type of testing ground where it seems possible to formulate new hypotheses on the relationship between physical and historical sciences. We therefore suggest here the development of a reflexive research dealing with the way we study ancient materials based on their nature, their specificity and induced impacts on analytical protocols, as a way to help structuring the development of methodological research on ancient materials.

3. Characteristics of the study of ancient materials

We will first attempt to highlight the main features of ancient materials in an heritage sciences perspective. We should at first clarify our meaning of the term “ancient materials”. Our idea is not to distinguish materials according to the period when they were produced, but to note that the historicity of these materials has an effect on their scientific study. We include jointly under their *historicity* their age, that renders the knowledge of their production conditions very uncertain, their modification by man, and their aging, which has altered their physical condition. As such, the “ancient materials” that allow putting more clearly in evidence the characteristics sought for date back to several centuries or more. However, there is no exclusive, ancient materials can theoretically be any material *seen from the viewpoint of its historicity*, and most observations made will also apply to very contemporary materials. In reality, the historical nature of the alteration of materials is such that there is not a frontier, but rather a continuum between

materials that have been more affected by their history and others that have been less affected at least for now.

3.1. A posteriori examination

It may seem an obvious statement, but only can we study directly materials that have survived their complete “disappearance”, therefore giving to the examination of ancient materials an *a posteriori* character. Most of the studies require reconstructing past states in the object history. As noted separately by Paul Philippot [22] and Laurent Olivier [23] at macroscale, this does not mean questioning a single isolated state but a continuum of piled-up states that are constitutive of the material itself. In addition, differences in degradation behaviours leads to taphonomic biases that may be particularly difficult to detect at the macroscale, and probably similarly at the microscale.

Reproduction of model materials to test specific properties and contribute to identify past states from artificial ageing also faces major theoretical and practical difficulties [24]. Approaching ancient materials with model materials would require a precise knowledge of their physico-bio-chemical history – from process to alteration – which is largely unknown and often *the aim of the study itself*. Even if all the requested information was known, the sensitivity of the systems under study to small fluctuations of the “initial” conditions and the physico-chemical context still makes extremely arduous their approximation through the reproduction of the different steps of their life cycle. The thermodynamics and kinetics of their evolution are so complex that we can consider that many systems follow a deterministic chaotic behaviour. This does not mean, far from it, that we cannot benefit from reproduction experiments, but rather that long-term behaviour laws will have a stochastic nature which landscape needs to be delineated.

This impossibility to observe ancient materials for a sufficient duration and to reproduce them *ad libitum* leads to the fact that many assumptions are *not testable* in a timeframe compatible with human research activities. Research strategies therefore differ greatly from those adopted in other fields of research, particularly those where the physical properties of materials can be optimised inline with the characterisation process. As pointed out 150 years ago by Claude Bernard as he was defining the experimental approach in Medicine, the researcher is constrained to an *observation* position around which he builds his scientific method (Fig. 1) [25]. In our systems, this observation approach is usually the starting point of an analysis of the material *as is* (French: *tel quel*).

3.2. Digging into ancient materials: an unrepeatable experience?

If the pathway from a past state of a material to its current state cannot be easily reproduced, even the experiment itself may be irreproducible. This intrinsic difficulty to repeat experiments on ancient materials is evident when the rarity or uniqueness hampers further sampling or characterisation of objects, particularly in the case of valuable artefacts from historical collections.

In addition, any measure leads to physical perturbations of the system under study. Photons are neutral particles and may be less directly damaging than electrons or ions. However, photoelectrons generated through UV and X-ray photo-excitation can lead to bond cleavage, radical formation, non-radiative processes (heat). Potential damages are particularly important in the soft X-ray range due to the high photo-ionisation cross-sections at these energies. Due to the load of energy deposited when performing synchrotron spectroscopy and imaging, there is a risk of degradation of the materials under study. Application of high doses is often all the more necessary that the sensitivity of currently available detectors is limited, especially in the X-ray domain. Damage can sometimes be visible

² For an overview on the relationships between technology and methodology in the historical sciences, see [20], in particular [21] which discusses Bruno Latour's position that “we have the social theory of our technologies”.

(to the Human eye): formation of color centers in glass, browning of organic compounds, *etc.* We also identify as a major analytical risk the potential loss of information, or worse the retrieval of misleading or biased information, from an area damaged by radiation, even without direct visual consequences to the sample or object. A range of precautions is usually taken to mitigate this risk but the possible deterioration cannot be excluded from our mind, all the more than we lack long-term experience about this impact.

Objectively, the beam is usually not the main cause of deterioration of samples. Preparation steps can lead to unintended (during polishing, handling or laying of the sample in particular) or voluntary (resin impregnation for easier cutting) contamination or alteration. Mechanical and physico-chemical constraints applied during cutting, polishing, marking, handling, *etc.* can significantly alter samples. The mere exposure to air of internal parts of an object can lead to chemical reactions, such as oxidation, which may not have taken place in the absence of sampling. One can wonder about the chemical condition of historical cross-sections which constitute fragile yet essential research archives in museum laboratories.

One can therefore draw a comparison between excavation at an archaeological site and into the material, both *unrepeatable* experiences [23,26,27] and probing for “a practical and moral requirement to extract the maximum possible information” [4]. This aim is usually pursued by combining observations from several analytical methods to form a body of evidence employing *multimodal* analytical sequences.

3.3. Heterogeneous materials

Unlike many modern and contemporary manufactured materials (synthetic polymers, high purity metals, glasses and ceramics, *etc.*), ancient materials are often particularly heterogeneous from the centimetre to the nanometre. Raw materials under consideration, whether from biological (protein glues, resins, wood, textile fibres. . .) or mineral (pigments, metals, earths, stones. . .) origin, were particularly heterogeneous already. Transformation during the “life” of the material by heating, mechanical constraints (hammering. . .), hydration in wet/dry cycles, chemical reactions, *etc.* will often add more heterogeneity to the material. Ageing and long-term reactivity with the environment may introduce considerable physico-chemical perturbations.

One should note here the polysemy of the term *heterogeneity* in its daily usage that covers three concepts:

- that of the compositional diversity of a mixture. Taking as example the elemental composition, samples are often described as containing “all the periodic table” leading to complex XRF (acronyms and techniques are summarised in Table 1) spectra with “a forest of peaks”. This chemical diversity extends far beyond the mere elemental composition. For instance, inorganic and organic compounds where mixed can react to form hybrid compounds (adsorbates, soaps, *etc.*). Even by looking at a single chemical element, its speciation can result from a local mix of species (with different oxidation states or atomic environments);
- that of the contrast in abundance. Taking as example elemental composition, concentrations of interest will vary from ppm (or lower) levels to 100%. Measuring ppm levels in (μm)³ volumes requires detecting femto- or even attogram abundances, therefore requiring sufficiently high emission cross-sections and a great efficiency of the analytical chain. Measuring elemental concentrations from traces, minors and majors is requested to attain quantitative information. This requires covering an abundance range that extends over 6 (or more) orders of magnitude. For this reason, methods will need to be at the same time sensitive to

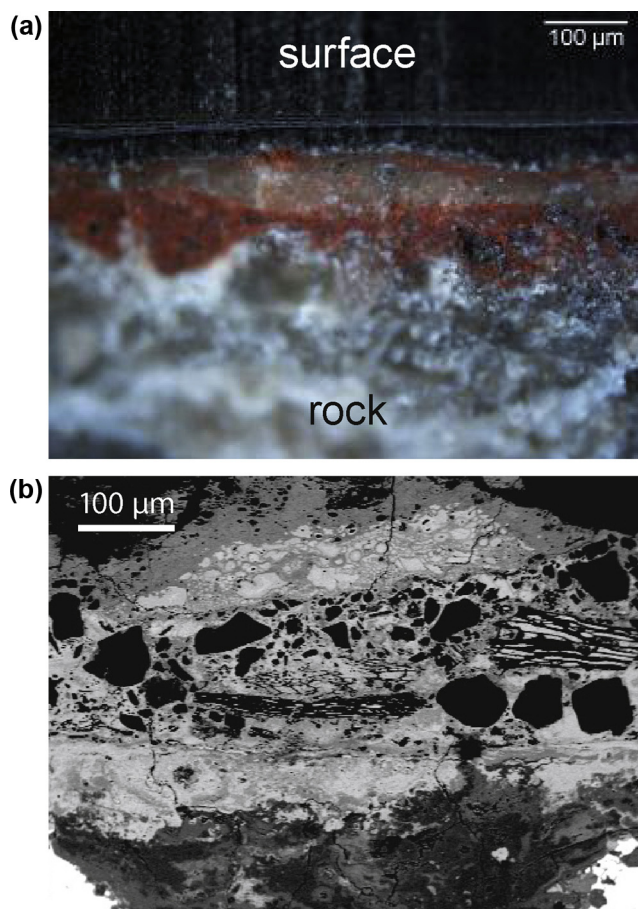


Fig. 2. Examples of ancient materials illustrating their spatial heterogeneity at the 1–100 μm length scale. Stratigraphies from (a) a rock art paint cross-section (image courtesy: St. Hoërlé), and (b) a corroded mediaeval nail (image courtesy: S. Réguer). Heterogeneity in these materials extends from nanometric to macroscopic length scales.

low amounts and should not saturate with majors, by covering *dynamically* a wide range of detection;

- that of the multiscale spatial topology. If the chemical composition of materials often results from mixtures at a point of analysis, it can also vary greatly from one point to another of the sample, or from sample to sample in a corpus. Systems appear frequently stratigraphic, inclusionary, textured, anisotropic, interfacial (Fig. 2). Compound distribution can generally be characterised by characteristic length scales of heterogeneity. In cases as distinct as the corroded surface of a metal object or the paint layers of an easel painting, heterogeneity may be present along more than seven orders of magnitude from the nanometre to the centimetre. Spatially-resolved methods inform on the materials at these different levels. Taking into account sets of objects (*corpus*) aside individual objects is often a methodological challenge.

This practical meaning of the term *heterogeneity* – at the same time relating to and often mixing composition, abundance and topology – leads to a main impact on the spectroscopy and imaging of ancient materials: the need to analyse a material at its different scales, attaining both ends from traces in a mixture to the majors in which they are embedded. Heterogeneity thus leads to the crucial character of the concept of scale and its variation, which is fundamental to allow building a coherent approach to such complex systems. These levels of complexity strongly orientate all characterization protocols and will be discussed in Section 5.

Table 1

Main synchrotron methods used to study ancient materials, physical origin and level of information obtained.

Physical origin	Characteristic transitions from core electronic levels	Density and compositional contrast	Probing of outer shell electronic levels	Excitation of bond vibration and rotation modes	Reflection on atomic plans
Main information provided	Elemental composition	Morphology, porosity	Coordination spheres, molecular organisation, Structural defects, Impurities	Molecular bonds, conformation	Structure, texture, mesoscopic organisation
Primary methods	XRF	μ CT	XAS	FT-IR	XRD
Secondary methods		Laminography	UV/VIS, STXM		SAXS

XAS: X-ray absorption; XRD: X-ray diffraction; XRF: X-ray fluorescence; μ CT: micro-computed tomography; STXM: scanning transmission X-ray microscopy; SAXS: small-angle X-ray scattering.

4. A few words on the synchrotron analysis of ancient materials

Synchrotron methods are based on the detection of particles (photons, electrons, ions) resulting from the interaction between light (photons) and matter [28,29]. We present here a brief introduction and invite the reader to consult recent reviews on the synchrotron examination of ancient materials [13–15,19]. The synchrotron light source is used in conjunction to laboratory and portable instrumentation when energy tunability, greater signal-to-noise (S/N) or a higher spatial and/or spectral resolution are aimed at. Mechanisms of interaction between photons and matter lead to over 50 analytical methods implemented at synchrotron facilities. In ancient materials studies, the main synchrotron methods in use inform about the elemental composition from major to trace elements (XRF, Table 1), the local electronic and magnetic environment and in doing so chemical speciation (X-ray absorption, photoemission, infrared and UV/visible spectroscopy), the structure and texture of organised compounds (X-ray diffraction and scattering) and the morphology (X-ray microtomography and related 3D techniques) [17,30].

4.1. Specificities of synchrotron analyses in ancient materials studies

The specificities of synchrotron radiation complement those of portable and laboratory sources [13,14]. Clear limitations are the pressure in terms of access to beamtime, and the need and costs to transport samples and objects to the large-scale facility. We retain here four of the major analytical characteristics in turn connected to the central specificity of the synchrotron source to emit a high flux of photons in a small solid angle (extreme *brightness*), this continuously over a wide spectral range (*energy tunability*):

- the radiation generated at synchrotron bending magnets and undulators covers a wide energy range from the terahertz to the hard X-rays with the ability to access one or two decades in energy at each beamline. This dynamic in excitation energy allows overcoming the discreteness of the main laboratory photon sources (X-ray tubes, monochromatic UV/visible lasers). It facilitates the coupling (multimodality) of several techniques on the same endstation, sometimes accessible at the same sample spot;
- the broad energy distribution and the beam intensity provide versatility to select the appropriate energy and excite distinct elements or compounds to decorrelate the signatures in presence. A high spectral resolution in excitation energy is made possible by using (crystal, grating) monochromators, even in the hard X-rays which is a specificity of the synchrotron source. This allows chemical speciation in synchrotron X-ray absorption, photoemission and UV/visible spectroscopy by probing speciation-dependant

energy states close to the Fermi level. More selectivity may be attained by restricting the energy bandwidth on the detection side using wavelength-dispersive setups in XRF, crystal analysers in XRD, emission filters and gratings in UV/visible spectroscopy;

- the intensity of the source, jointly with optimised optical and instrumental characteristics at synchrotron end-station, will generally lead to a S/N ratio orders of magnitude greater than that attained at laboratory light sources;
- the high intensity allows performing:
 - micro- or nano-spectroscopy even though many photons may be lost due to the absorbance and limited acceptance of focusing optics,
 - full-field imaging where the sensitivity of a pixel is proportional to its surface, therefore requiring a trade-off between pixel size and the counted intensity.

4.2. Focused spectroscopy and full-field imaging

Cultural heritage and archaeology studies mostly exploit the micro-focused spectroscopy capabilities of synchrotron beamlines either in spot analyses or raster-scans [10,31]. In the following, we will distinguish between *mapping* (or *raster-scanning*) spectroscopy i.e. the measurement of spectra from adjacent regions of a sample achieved by moving each region into the photon beam, sequentially or continuously in a *flyscan*, and (full-field) *imaging* (or *microscopy*) where an image of the sample is focused onto a detector and the signal coming from each region of the sample is measured at each pixel simultaneously [14,32]. In addition, a hybrid approach also exists where raster-scanning is performed with a 1D or 2D array detector and the collected data are stitched together (Fig. 3).

Raster-scanning allows the collection of 2D data at identical spectral quality than for single spectra. Scanned spots can also be non contiguous to map large objects using *sub-sampled* fast macro-scanning. Paintings were recently macro-scanned using XRF and XRD to determine pigments distribution over their whole surface [33,34].

4.2.1. Micro- and nanofocused spectroscopy

The high brightness of the synchrotron beam allows implementing micro- and nano-beams in the IR to X-ray range, while maintaining a reasonably low divergence, thereby providing a high spatial selectivity. The development of X-ray micro- and nano-focusing optics is challenging as the optical index n of most materials is close to unity in the X-ray range, and has been a field of major instrumental development since the late 1990s. For our concern, microspectroscopy setups are optimised to provide both: a high spectral resolution in emission arising from optimised geometry, optics and electronics of the detection chain; and a large dynamic range to allow collection of complex fingerprints from a single compound and/or of several fingerprints from distinct compounds. It should soon be possible to implement

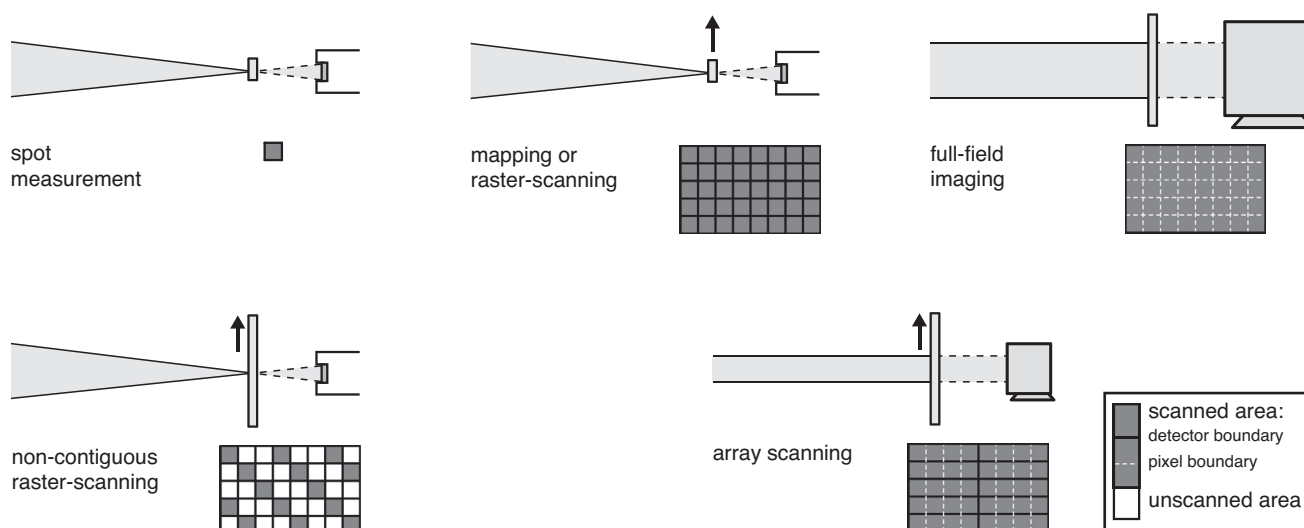


Fig. 3. Main data collection modalities discussed: spot measurement, mapping or raster-scanning and fullfield imaging. Non-contiguous raster-scanning is used for the fast macro-scanning of large objects at a spot size smaller than the scanning step size.

focused spectroscopy at a spatial resolution of a few nanometres, the current resolution limit being in the 30–50 nm range in the medium/hard X-ray. This development is mostly stimulated to address needs in life and nanosciences, and nano-resolved methods are still struggling to break through in ancient materials studies, except in very specific cases. This can be explained in part by the fact that our understanding of the complexity of these materials at the micrometre scale is already in most cases lacunary. Interpretation of the data collected can therefore result particularly difficult if not impossible. Statistical representativeness is a central issue, as studying at a resolution of $50 \times 50 \text{ nm}^2$ an object of a total surface of $50 \times 50 \text{ cm}^2$ typically represents a $1:10^{14}$ surface ratio. Special attention needs to be paid to avoid over-interpreting spatially-localised observations. In addition, nanofocused characterisation methods may impose very strong constraints on the preparation, handling, storage, etc. of samples. As already mentioned, the high density of flux is a source of potential alteration.

4.2.2. Full-field imaging

Until recently in ancient materials studies, synchrotron full-field imaging techniques were mainly limited to the X-ray μCT imaging of paleontological specimens. These techniques are in very strong development suggesting many new applications to the study of heritage micro-samples and objects. In our context, the quality of the full-field imaging chain is mainly characterised by: a large image size providing large spatial dynamics and; a high spatial resolution resulting from a small point spread function and a large numerical aperture. In addition, the quality of the transport of the optical signal from the sample to the detector is essential to maintain spatial characteristics. Full-field imaging allows greatly decreasing the repositioning times of samples during experiments, particularly at the submicrometric scale, where ensuring that the correct zone is imaged may be a tedious and time-consuming task that perturbs the sample (marking, laying on TEM grids. . .).

Micro-focused spectroscopy and full-field imaging therefore appear as complementary approaches characterised by optimised spectral and spatial data collection respectively. A consequence is the interest to combine both approaches to benefit from the respective strengths of each. For instance, at a synchrotron XAS beamline, XRF spectra can be collected at a few selected excitation energies near an elemental edge of interest to determine the regions of interest where local absorption spectra can be acquired.

Conversely, collection of full spectra allows determining optimal emission/excitation conditions for full-field imaging. This complementarity can be facilitated by appropriate control and monitoring strategies.

5. Traces, majors and dynamics

We will discuss here the impact of the intrinsic heterogeneity of ancient materials during their synchrotron characterisation, identifying three main practical consequences: the interest of the study of *traces*, that of *majors* and the *multiscalar dynamics* between both endpoints.

5.1. Traces

In many heterogeneous ancient materials, the recovery of evidence is based on “tiny amounts” and we could call here the notion of *trace*. As noted earlier for the term heterogeneity, the trace includes polysemically the analysis of individual fingerprints (requiring *high selectivity*), that of very low quantities of matter (*low detection limits*), that of localised anomalies (*high spatial resolution*).

For fifty years with the advent of neutron- and X-ray based analytical methods [1,3,35], a particular effort was made in conservation sciences and archaeometry towards the determination of the so-called *trace elemental* composition, using methods such as chemical analyses, Nuclear Activation Analysis, Inductively Coupled Plasma-based spectrometry, Energy Dispersive/Wavelength Dispersive-XRF and Particle induced X-ray emission (PIXE) applied to the determination of limited elemental amounts particularly in homogeneous materials [4,30,36,37]. Following an elemental signature from a geological deposit to a gem, an obsidian or a gold artefact may allow to infer its origin and to draw exchange and trade routes of products or semi-products [1,4,36,38]. Historically, early synchrotron analyses of archaeological materials, using XRF, were influenced from PIXE, with trace elemental quantification identified as the major target [39–42]. The concept of trace elemental content is particularly suited to objects distinguishable not so much from their average elemental composition dominated by major elements, but from small *deviations from their expected average composition*. Beyond the trace elemental composition, deviations from the expected average behaviour can be extremely diverse in nature: trace mineral phases [43], crystal defects [44], limited presence of oxidised/reduced compounds [45], etc. Salvadò et al. noted

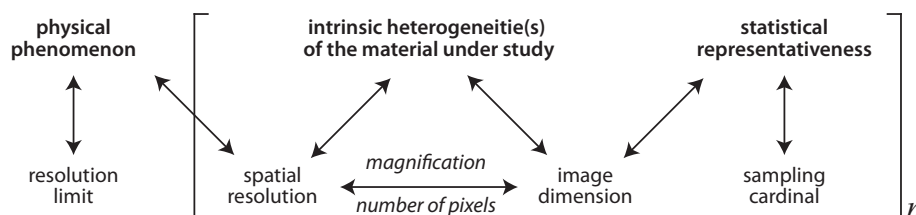


Fig. 4. Graphical representation of the relationships between length scales from the physical phenomenon to statistical representativeness, and corresponding instrumental parameters.

the presence of crystalline trace phases in copper-based green pigments in cross-sections from a painting of the Catalan gothic painter Jaume Huguet (*ca* 1415–1492) and underlined the importance of these trace minerals as markers of the technology used to prepare these pigments and of their alteration [43]. We see here an *extension of the concept of trace*, beyond the trace elemental information to any distinguishable compositional singularity that needs to be addressed by a suitable analytical sequence.

In complex mixtures, selectivity is requested in order to be able to measure unique spectral fingerprints. Detection of *trace* features buried in intense signal from the matrix will require specific strategies, for instance based on the optimisation of the excitation energy. Here, the tunability in energy of the synchrotron beam is of clear interest.

In parallel, critical information is often nested in spatially-localised anomalies at microscale: inclusions, clusters, grains and aggregates, strata and their interfaces, *etc.* These spatial anomalies might provide information on past technologies and alteration mechanisms. They can lead to specific material properties (for instance mechanical properties related to the presence of localised crystalline defects) or form specific centres of reactivity, potential nucleation centres of neoformed phases in the course of redox processes. Microprobes from easier-to-focus charged particles brought (and still bring) essential contributions through electron microprobe, μ PIXE/PIGE, *etc.* Focusing X-ray beams is far more complex and only in the last 10–15 years, synchrotron analysis could lead to essential contributions in microanalyses. Using standard far-field techniques with an incoherent illumination, the ultimate size of the objects that can be differentiated is constrained by the diffraction limit.

In many cases, all meanings of the trace need to be taken into account simultaneously. For instance, the determination of the trace elemental composition of selected fayalitic microscopic inclusions by confocal μ XRF may allow specifying the origin of mediaeval iron artifacts for which demonstration of provenance was shown to be of major difficulty if not impossible from macroscopic contents [46].

This notion of trace is essential as it governs research strategies on a concrete viewpoint, directly within the design of the experiments, and also appears equally as a key concept in Humanities since Ginzburg's *evidential paradigm* and his suggestion to consider enquiry as a model of the scientific process in the early 1980s [47].

5.2. Majors

The definition of traces implies in a reciprocal manner that of their complementary environment. The trace information that is looked after is hidden in a matrix, among majors. Analysing majors is generally less regarded as an issue. However, the synchrotron source and instrumentation may here impose specific constraints. An example is the low divergence of the synchrotron beam that will constrain the beam size in X-ray analyses, when a large footprint is desired. Under an abundance meaning, majors will often lead to saturation of detectors. Degrading the bandwidth in excitation or

emission may be impossible as it results from selection of major optical components of each beamline.

5.3. Dynamics

Co-characterisation of traces and majors is often needed, and will require sufficient dynamics. This is for instance the case to attain quantification through matrix corrections in X-ray analyses by:

- co-characterising between both endpoints, even though (spatially) the traces may be visible only at high resolution in a slowly fluctuating matrix composition, or (spectrally) traces may be orders of magnitude lower in concentration than majors or minors;
- obtaining complementary information from other instrumental means;
- modelling the matrix composition. As for the previous two notions, this question of dynamics also concerns simultaneously the compositional diversity (addressed by analytical *versatility* and *multimodality*), multiscalar abundance (*wide dynamic range*), and multiscalar topology (*wide spatial dynamics*).

Regarding the compositional diversity, the versatility of the synchrotron source is here of specific interest. The energy tuning range attained at a single beamline allows studying several chemical elements or absorption edges. Coupling of several methods can also be done at beamlines.

Dynamics in terms of abundance is often an insufficiently discussed issue. Having access to intensities from traces to majors is often a problem due to the limited dynamic range, that may lead to insufficient S/N ratios or saturation of detectors. Specific strategies involve filtering the response from majors, by using metallic foils in synchrotron XRF and XAS for instance, defining specific energy thresholds for detectors, using dichroics and gratings to decrease the contribution from scattering in UV/visible spectroscopy, *etc.*

The most frequently mentioned characteristic of ancient materials is their multiscalar organisation from the nanoscale to the macroscale. Interestingly, the term *spatial dynamics* is not of frequent use, possibly due to the too recent availability of large size detectors for material analysis. We can distinguish three main sets of length scales to characterise the heterogeneity: that of the physical phenomenon studied, those of the heterogeneity of the material and those of the statistical representativeness of the study (Fig. 4).

These scales depend on the question, the material, the analytical technique used and the property studied: elemental composition, oxidation state and nature of coordination spheres, structural defects, mineralogical structures, grain size, degree of polymerisation, texture (specific orientation), *etc.* Heterogeneity length scales influence the selection of the optimal spatial resolution(s). Distinct scales of heterogeneity and representativeness may be associated to the distinct physical phenomena studied in the same sample, for instance a sample can be homogeneous at microscale in terms of elemental composition but of heterogeneous mineralogical composition (crystalline phases) at the same length scale. A powder

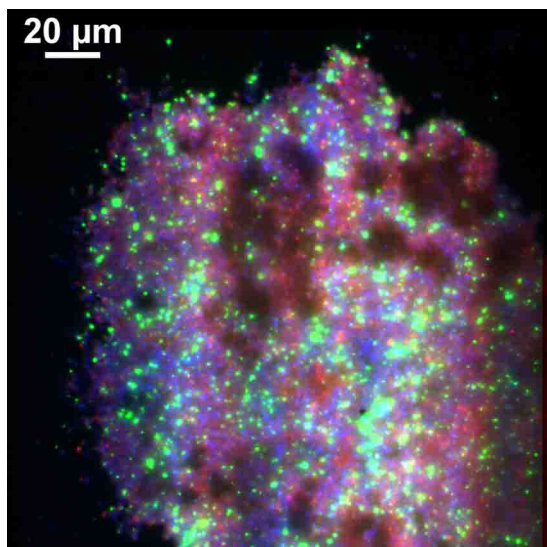


Fig. 5. False-color full-field photoluminescence image showing the strong defect-related heterogeneity of a ZnO pigment from the Forbes historic collection (inv. 1.06.529; red channel: 550 nm, 20 nm FWHM; green: 465 nm, 30 nm FWHM; blue: 380 nm, 15 nm FWHM). Excitation wavelength: 280 nm. Data collected at the Telmos endstation, DISCO beamline, SOLEIL.

of the pigment zinc white ZnO may be homogeneous in elemental composition as seen in X-ray fluorescence or SEM-EDX, but have a significant spatial heterogeneity at the micrometric scale in terms of crystal defects observed in synchrotron UV/visible photoluminescence imaging (Fig. 5).

The dimensions and number of areas analysed (sampling cardinal) need to be optimised based on the issue addressed. Moreover, the individual object is often not the adequate level of representation to extract relevant behaviour laws. Ancient materials often take their full historical significance when considered within corpus or collections of objects, and compared with modern reference material or aged materials that tentatively model ancient ones. The sampling cardinal is usually a very constrained parameter in terms of availability (sample preparation, limited number of samples), instrumentation (dead time of detectors, movement of stage motors, surface of the detectors, change of samples), and induces further processing costs.

6. Methodological perspectives

Our observations lead to several concluding epistemological remarks. They may seem to provide a simplistic framework on the study of ancient materials, but they already lead to methodological and operational implications by taking into account more realistically the specificities of the systems at stake.

6.1. Studying traces

The above distinction between amount, compositional and topological characteristics, corresponds to intrinsic variables such as *concentrations* in the various compounds and *spatial distributions*, taking into account the cross-sections and yields of the modalities of interaction between photons and matter. The observable to which one has usually access during the experiment is the intensity of the collected signal resulting from the interactions between light and matter, taking into account the geometrical configuration. In the case of synchrotron-, or more generally photon-, based studies, the final aim of the experiment is often to obtain an information about the material composition, through solving inverse problems of matrix correction and further using this

information to solve another inverse problem, that of identifying past states and processes that led to the currently observable state of the material (initial raw material, operating sequence, alteration). Spatial and spectral characteristics can, to some extent, be paired by experimental parameters such as position and beam size on the one hand, excitation/emission energies on the other hand. This is indeed a schematic representation as the spatial and spectral characteristics are mixed, for instance in speciation or structural studies. In addition, trace amounts can produce major spectral responses when the yield of the response varies significantly among compounds.

Selection of the primary conditions of observation requires an initial expectation of the result to be obtained, based on a *a priori* knowledge. The *trace* often appears as an *unforeseen* singularity in this experimental process. Basically, it appears as an irregularity, whether quantitative or spatial, in relation to an expectation. It is therefore both an intrinsic property and the result of an observation, thereby constituting a fundamentally relational concept between the object, its past and the scientist. This leads to several consequences:

- the trace constrains the observer to turn its sight to unexpected grounds in exploratory approaches;
- the search for such singularities requires a sufficient broadening of the range of analytical conditions or they may be missed out;
- this broadening means using methods with as limited presupposed information as possible;
- coupling measurements in *multimodal* characterisation sequences that allow incorporating information on the material previously acquired through other experimental means, with an impact on the amount of documentation to store and analyse.

This may partly explain why spectroscopic methods providing somewhat “rough” data – such as FT-IR, UV/visible spectroscopy or multi-elemental XRF – appear so powerful and robust. These methods require far lower *a priori* knowledge than, for instance, most separative methods. They therefore participate to a holistic study of ancient materials.

6.2. Spatial dynamics in synchrotron spectral imaging

The information sought for will partly be found in the local *quantitative* data (in the *trace* chemical composition for example), and in the *spatial distribution* of this data. The spatial distribution of data from ancient materials is in fact often more informative than precise quantitative measurements. This is especially true when the uncertainty of experimental methods, taking into account matrix and morphological corrections, makes it difficult if not impossible to attain quantitative information.

For instance, visualisation of the layered build-up in paint cross-sections is often more or equally informative regarding the artistic or technological gesture than the accurate local determination of the content in one of its components (binder, pigment, etc.). This can be illustrated by our observation of traces of earth-based pigments in the stratigraphy of the varnish of a theorbo from M. Dieffopruchar [48]. Here the FT-IR spectral signature, even observed with the high brightness of the synchrotron source, is so faint that only the spatial consistence of this signal over a whole stratum confirms the mere presence of the compound in the varnish stratigraphy (Fig. 6). Identification was further corroborated with elemental and light microscopy information. Similarly, for the study of the corrosion of metal archaeological artefacts, spatial information such as corrosion facies, the percolation of phases or the connectivity of the pore network allowing circulation of fluids and gases are critical [49,50]. The spatial distribution of iron hydroxychloride $\beta\text{-Fe}_2(\text{OH})_3\text{Cl}$ domains in corroded iron objects by synchrotron

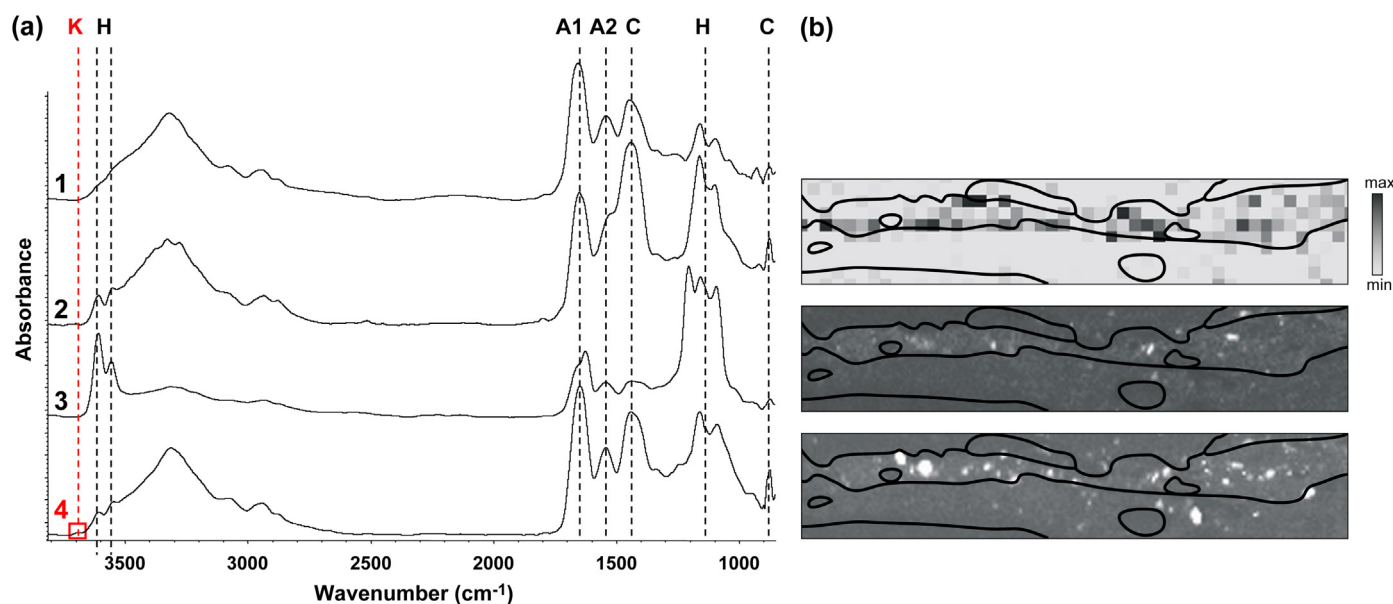


Fig. 6. Illustration of the coupling of spectral and spatial information to identify a pigment in the varnish layer of a theorbo by Magno Dieffopruchar, late 16th c., Venice (coll. Musée de la musique, E.980.2.321) through synchrotron Fourier-transform infrared (FT-IR) microspectroscopy: (a): typical SR-FTIR spectra corresponding to a pixel of layer L1 characteristic of a proteinaceous material (1), a grain of calcium carbonate (2), a grain of calcium sulphate hemihydrate (3) and a grain of the “earth” material in layer L2 (4). In the latter, note the spectral feature marked with a red box, where a low-intensity contribution is attributed to the OH stretching of kaolinite centred at 3698 cm^{-1} ; (b): from top to bottom, map of synchrotron FT-IR signal integrated in the $3715\text{--}3679\text{ cm}^{-1}$ range, Al and Si SEM/EDX elemental maps. Synchrotron FT-IR data were collected at the ID21 beamline, ESRF, Grenoble [48].

Table 2

State of development and implementation of synchrotron focused spectroscopy and full-field imaging: (t) in test, (+) in operation, (++) regularly available and used.

Method	Focused spectroscopy		Full-field spectral imaging	
	Nano-	Micro-	Multi-	Hyper-
FT-IR	t	++	–	+
UV/vis spectroscopy	t	+	+	t
XRF	++	++	t	t
XAS	++	++	t	t

X-ray absorption methods resulted in a rereading of corrosion mechanisms of iron archaeological artefacts in soils; these conductive phases, even at trace levels, are likely to influence strongly the mechanisms of oxidation of metals in soils [49]. The fact that qualitative data may be more informative than quantitative ones may seem counterintuitive. Indeed, most of the effort of early synchrotron works in the field was put into the quantitative determination of absolute elemental concentrations [40,41] and may account for the progressive shift observed towards imaging and raster-scanning modalities.

In our systems, the main parameters of interest (so far) have been excitation/emission energies and the spatial variables. Additional variables were occasionally introduced such as time and experimental conditions (temperature, E/pH potential, etc.). Raster-scanning and full-field imaging both allow to collect data of the kind $I(x, y, (z), \lambda_{\text{exc}}, \lambda_{\text{em}}, \dots)$, multipixel and multiband respectively. Approaches bridging the gap between those two and leading to synchrotron spectral imaging have started to emerge over the past years (Table 2), by two main means:

- from raster-scanning focused spectroscopy by speeding up the sample scan. Data collection duration increases linearly with the number of pixels N , and is several orders of magnitude greater in 2D and *a fortiori* 3D raster-scanning. Optimisation implies reduction of dwell and readout time, increase of the solid angles of

detection, the speed and stability of scanning motors, flyscan acquisition, etc.;

- from full-field imaging by adding more energy channels in excitation and detection: extension of the detection range, optimisation of the resolution, increase in the dynamics of excitation and detection systems (monochromators, optics, gratings, detectors). Here, the necessity to register images – to reposition them so that a single pixel of each image corresponds to the same actual area of the sample studied – is imposed by the chromaticity of detection chains.

With the systems available today based on micro-/nanoprobe setups, the size of the spectral images generated will typically cover a spatial dynamic of 2–3 orders of magnitude. This amounts to cover a characteristic length of $50\text{ }\mu\text{m}$ at a projected pixel size of 50 nm , and leads to megapixel images. The increase by one order of magnitude will lead to images that cover continuously from 100 nm to 1 mm . This development is under way for complex materials – for instance, Ryan et al. recently obtained 76.8 megapixel XRF images covering 12 mm at a spatial resolution of $1.25\text{ }\mu\text{m}$ of a calcite ore, scanned with a fast-readout large solid angle detector [51]. The distribution of pigments across entire paintings was also imaged with a coarse mesh by XRF/XRD macro-scanning [52]. In parallel, new developments emerged from full-field imaging setups primarily based on new detectors (CCDs, CMOS, photon counter area detectors). A MCT Focal Plane Array (FPA) detector was recently implemented at a synchrotron infrared beam-line [53]. The potentials of UV/visible spectral imaging were explored using EM-CCD detectors coupled to a filter wheel [44]. Synchrotron full-field XRF imaging of small objects at a spatial resolution of $50\text{ }\mu\text{m}$ over an imaging area of $12.7 \times 12.7\text{ mm}^2$ was reported with the coupling of a camera obscura and capillary-based setups to a pnCCD detector sensitive in the 3–40 keV range [54]. A full-field setup was developed at the ID21 beamline of the ESRF using a CCD detector to collect complete spectral 2D-XANES datasets [55]. Hard X-ray area energy-resolved detectors are still constrained in terms of

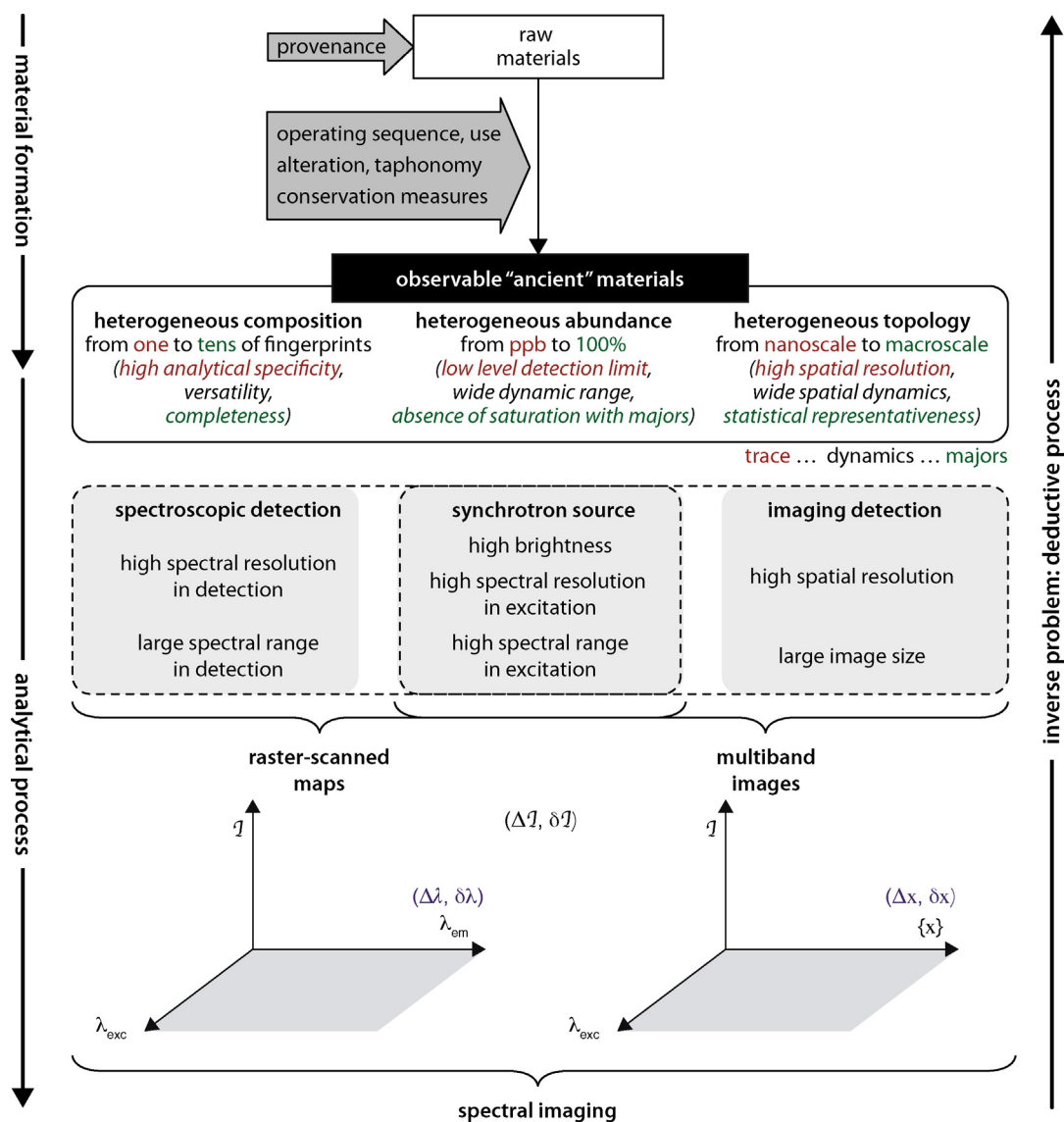


Fig. 7. Scheme summarising the main parameters at stake in the study of ancient materials using photon-based micro/nano-spectroscopy and full-field imaging.

sensitivity, spatial and spectral resolution, as well as spatial and spectral dynamics, but are under intense development.

In summary, spectral imaging provides:

- locally, access to low detection limits, high spatial resolution and high spectral specificity;
- globally, the analysis of major compounds, access to the macroscale, and simultaneous collection of numerous fingerprints;
- intermediately, they embrace simultaneously successive length scales and provide some level of versatility on the breadth of compounds detected.

The spatialisation of the data in spectral imaging therefore seems to be a way to address the multiscale spatial character and the relevance of traces and majors in ancient materials. Dynamics appear central here. If what happens precisely at the local scale is inaccessible or does not bear enough information, and what happens globally is also often inaccessible, there may be intermediate length scales to which we have access. One can then state for instance that: "the edges of pigment grains are more oxidised than their bulk", or "the borders of the pores are generally

leached out" and so forth. More than the relevance of macroscopic or microscopic studies, we could speak here of that of *mesoscopic*³ studies for which further development of detectors is central. As a consequence, isolating one length scale, be it nanometric, seems somewhat less critical than attaining sufficient dynamics of information at the various characteristic length scales (Fig. 7).

6.3. Improving jointly separation and identification

When the spatial resolution attained by spectroscopic imaging is comparable or greater than the characteristic length scale of the intrinsic heterogeneity for the property studied, certain pixels may lead to spectra that are direct characteristic fingerprints. Even when this is not the case, the level of discrimination of the compounds in presence can be improved through combining information from sometimes coarse or noisy spectral data with their localisation at high spatial resolution. Imaging thus allows taking benefit from the local *in situ* segregation or aggregation of chemical compounds – in turn reflecting the intrinsic and

³ The term *mesoscopic* is here taken at a greater length scale than in nanosciences.

extrinsic history of the material. The spatial separation observed *in situ* in artefacts is inherent to the physico-chemistry of compounds taking into account: the characteristics of the raw materials; pre-depositional actions and; post-depositional processes (taphonomy, impact of the extraction from the depositional context, restoration, conservation and storage) [14]. They therefore reflect the thermodynamic and kinetic behaviour laws that governed obtention of the observable state of the material during its geochemical formation, manufacture, alteration and/or treatment. Human gestures in operating sequences are crucial here: the sorting out of materials, film deposition processes in painting or ceramics, the mechanical work of metal, etc.

In the spectral imaging of ancient materials, the topology underlying the data carries useful information. The spatialisation of the data therefore allows contextualising the data and defining (spectral, spatial) signatures that can be processed using chemometrics in the $(x, y, (z), \lambda_{em}, \lambda_{exc})$ hyperspace. However, discriminating is not identifying: distinguishing various fingerprints does not necessarily mean that the data are sufficient to identify corresponding compounds. For example, we can distinguish the layers from a stratigraphy and be certain that their composition differs without knowing precisely in what physico-chemically [44]. Reciprocally, inferring the existence of an underlying partly unknown structure of the data – a *hidden model* – can in itself contribute to refining the spectral information. “The image also tells us about the pixel”. Hypotheses can be postulated on the topology of the $(x, y, (z), \lambda_{em}, \lambda_{exc})$ hyperspace, for instance that spectra from neighbouring pixels are more likely to be similar except where there is a strong discontinuity: piecewise continuity of quantitative data and its derivatives, regularity of the shape of boundaries between strata, etc. Topological dictionaries could also be derived for classes of “comparable” materials. It then becomes possible to improve the segmentation of spectral maps by adding *a priori* information to take into account the topological information simultaneously with the spectroscopic data [13,56,57]. In an artwork, we may to some extent reintroduce the action (“*the hand of the artist*”, P. Walter) into the identification of pigments and alteration compounds. We are here, paradoxically, “injecting a part of qualitative data to refine quantitative data”. This dimension looks largely under-exploited and the current spectroscopic *praxis* usually considers individual spectra of the same map as if they were unrelated to one another.

6.4. On the historicity of ancient materials

In this discussion, as well as in our review of the literature from the past twenty years, several concepts have emerged recurrently: trace, scale, corpus, context, alteration. They seem to be elements of a formalised methodology underlying our scientific operations, without at the same time being a true explanation. The aim is here to clarify the implicit system formed by these notions, both to better formalise the experimental process, and to understand how these processes unveil an original point of view on physical sciences. In the approach proposed, the main originality comes from the fact that we confront Physics with the historicity and the singularity of objects, when these characteristics are usually put aside in the usual theoretical models of Science. It therefore seems necessary to conclude this contribution, by pointing the importance of a thorough work on these notions with an epistemological point of view.

This clarification has a dual aim. First, it would help to stabilise the conceptual vocabulary used. If the terms *trace* or *scale* are regularly used, their theoretical but also empirical significance often varies from one case to another, resulting sometimes blurred. Given this situation, the search for an epistemological and semantic core for a polysemic concept such as *trace* seems a fundamental

issue of research in our field. Why and to what extent can we use a term that refers jointly to a small amount and a physical mark? Similarly, the notion of scale and considerations on the distinct scale changes and the associated discontinuities seem a necessity to outline more clearly the contours of the experimental work. In fact, the stabilisation of the conceptual vocabulary and its accuracy has very practical consequences on our thinking about the instrumentation, the development of experimental procedures and the ways to report results.

The second objective of this clarification is part of a more general epistemological framework. These notions, as well as thinking about ancient materials as *heterogeneous*, subjects of an *as is* experimentation, or on the nonreiterability of science operations, eventually question the theoretical framework within which is inscribed our scientific approach. The classical framework of Galilean physics and their Kantian and neo-Kantian epistemological extensions prove ill-suited to describe here the construction of knowledge that deals with singularities. Instead, the historicity of these ancient materials, as well as the use of concepts such as trace, scale or corpus, or a methodology where, in the words of Claude Bernard, “one observation may serve as control to another observation” [25], that is to say with a “think by-case basis”, beckons to the epistemology of historical sciences, as it has developed over the last thirty years under the influence of Carlo Ginzburg [47] or Jacques Revel [58,59]. It is not to say that the physics of ancient materials is, simply, a historical science, but at least that its practice can raise extremely sharp theoretical questions to the whole discipline. It would be interesting – and it will be one of our aims [18] – to further explore the theoretical aspects of the encounter between the natural sciences and historical sciences in the field of archaeo- and palaeomaterials. Their apparent marginality and status of *boundary objects* [60] may make them more relevant than others for researchers to outline an epistemology that lies beyond the reducing clashes between natural and historical sciences that have often characterised the contemporary epistemology⁴ since the *Methodenstreit* of the late nineteenth century to the *Science Wars* of the late twentieth century.

7. Conclusions

The *a posteriori* framework of the study of *heterogeneous* materials considered in their *historicity* appears as a structuring parameter of the advanced spectroscopic and imaging study of ancient materials. Based on the main constraints encountered when studying them with synchrotron-based methods, the analysis of traces, that of majors and we suggest, more importantly, that of the dynamics extending between both endpoints appear as central concepts. On-going development of multimodal spectral imaging is expected to address some of the corresponding difficulties. This reflexive approach provides an original epistemological framework adapted to and nurtured from the multidisciplinary research on ancient materials and confronted to their analytical specificities. Future developments of such an epistemology will follow two main paths, one prolongating the suggested clarification of the vocabulary of the issues and of the scientific operations at stake, the other aiming at a sociological and historical depiction of the practical consequences of such constraints.

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⁴ For an interdisciplinary attempt to document this notion of scale, please refer to [61].

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