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Mitigation strategies for radiation damage in the analysis of ancient materials

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ABSTRACT

The study of materials in cultural heritage artifacts and micro-samples benefits from diagnostic techniques based on intense radiation sources, such as synchrotrons, ion-beam accelerators and lasers. While most of the corresponding techniques are classified as non-destructive, investigation with photons or charged particles entails a number of fundamental processes that may induce changes in materials. These changes depend on irradiation parameters, properties of materials and environmental factors. In some cases, radiation-induced damage may be detected by visual inspection. When it is not, irradiation may still lead to atomic and molecular changes resulting in immediate or delayed alteration and bias of future analyses. Here we review the effects of radiation reported on a variety of cultural heritage materials and describe the usual practice for assessing short-term and long-term effects. This review aims to raise awareness and encourage subsequent research activities to limit radiation side effects.

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Abbreviations: BM, Bending magnet; CT, Computed tomography; EDX, Energy-dispersive X-ray spectroscopy; EELS, Electron energy-loss spectroscopy; FT-IR, Fouriertransform infrared spectroscopy; IBA, Ion beam analysis; LA-ICP-OES/MS, Laser-ablation inductively-coupled plasma optical-emission spectroscopy or mass spectrometry; LA-TOF-MS, Laser-ablation time-of-flight mass spectrometry; ILBS, Laser-induced breakdown spectroscopy; MALDI, Matrix-assisted laser desorption/ionization; NAA, Neutronactivation analysis; NEXAFS, Near-edge X-ray absorption fine structure; NRA, Nuclear reaction analysis; PIXE, Proton-induced X-ray emission; RBS, Rutherford backscattering spectrometry; RD, Radiation damage; ROI, Region of interest; SAXS, Small-angle X-ray scattering; SEM, Scanning electron microscopy; S/N, Signal-to-noise ratio; STXM, Scaning transmission X-ray microscopy; TEM, Transmission Electron Microscopy; VUV, Vacuum ultraviolet; XANES, X-ray absorption near-edge structure; XAS, X-ray absorption spectroscopy; XRD, X-ray diffraction; XRF, X-ray fluorescence.

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1. Introduction

Analytical techniques that make use of intense radiation sources are applied to an increasingly large number of cultural heritage artifacts and samples. As a result, material alteration can occur. Radiation exists not only in a research environment but also as a natural component of our everyday life (e.g., the sun and artificial lighting, cosmic rays, radioactivity, and background radiation). Other processes can of course also cause damage to heritage artifacts; these materials are continuously degraded by physical, chemical and biological causes while on display, during travel, or in storage. Degradation due to these "natural causes" is inevitable as normal "wear and tear" but is also countered using specific mitigation procedures.

Intense radiation sources, such as synchrotron radiation (SR), ion beams, and laser sources, have become preferred approaches for the analysis of a wide range of archaeological, art and paleontological specimens. At ion-beam facilities, *in-situ* ion beam analysis (IBA) of cultural heritage objects using focused beams extracted to air has been a major breakthrough that can be coupled to advanced high-resolution measurements on samples in a vacuum environment.

The study of cultural heritage objects has largely made use of proton-induced X-ray emission (PIXE) analysis [1–5] and, to a lesser extent, a range of other IBA techniques, such as Rutherford back scattering spectrometry (RBS) and nuclear reaction analysis (NRA) [6,7].

In the X-ray range, synchrotron beams are orders of magnitude more intense and brighter than conventional laboratory sources. Synchrotron-based methods used in heritage sciences are now very diverse and provide, e.g.:

- elemental information through X-ray fluorescence (XRF);
- speciation, chemical and molecular information through X-ray absorption spectroscopy (XAS), scanning transmission X-ray

microscopy (STXM), UV/visible photoluminescence and Fouriertransform infrared spectroscopy (FT-IR);

- structural information through X-ray diffraction (XRD) and smallangle X-ray scattering (SAXS); and,
- morphological information through X-ray microtomography (μCT) [8–11].

At synchrotron facilities, recent developments include full 2D and 3D scanning of entire paintings and paleontological fossils (e.g., DESY, SSRL, ESRF, SOLEIL, and SLS), and many studies on unique microsamples of the highest historical value [12,13]. For synchrotrons alone, this has led to more than 700 publications, half of them within the past five years.

Laser sources are also increasingly used for cultural heritage characterization [14]. Spectroscopic and spectral imaging techniques are employed for obtaining chemical information from samples and artifacts [15–17]. Various interferometric and holographic techniques are reported for mapping stratigraphy, structural defects and deformation in whole objects and surfaces [18–20], while laserablation (LA) methods offer new ways of handling demanding problems in conservation and restoration of monuments and artwork.

In the following, we use the generic term "objects" to include both artifacts and samples. Indeed, conservation scientists mostly regard microsamples from ancient artifacts as an integral part of world cultural heritage. There is little doubt that many samples collected on artifacts and stored in museum science laboratories will be studied in the years to come to provide unique information without further sampling of the original artifacts.

As the use of intense radiation sources has increased for the analysis of a wide range of cultural heritage samples, the associated risk of radiation damage to them has become a subject of discussion in conservation communities. There is potential for damage with such exposures, as risk increases with exposure. However, unlike in living systems in which radiation-induced damage may readily be repaired by living cells, in cultural heritage materials, there is usually no such self-healing mechanism, and, beyond a certain threshold, the damage will be significant and irreversible. While this trend is observed, there is no consensus on measures to be taken to minimize associated risks, except to lower exposure to radiation as much as possible.

The number of publications detailing damage from intense radiation sources is very limited and the terminology regarding damage to cultural heritage artifacts needs to be refined. It is therefore timely to introduce a more efficient terminology and to review and to address the question of mitigation strategies for radiation damage to cultural heritage materials. In this article, we therefore

- 1 propose a new definition of radiation-induced effects in cultural heritage materials that goes beyond that based on immediate visual inspection;
- 2 identify relevant activities in the field and neighboring areas that provide valuable information on damage mechanisms to diverse cultural heritage materials;
- 3 propose mitigation strategies; and,
- 4 review monitoring and recording strategies.

We consider that there is a need to define a new area in which research on damage mitigation, assessment and fundamental laws of alteration can be performed without sending over-alarming messages on analyses that will not result in visible nor structural alteration.

2. Definition of radiation damage to ancient materials

2.1. Visual damage ...

In the field of cultural heritage, the common definition of damage is mostly based on an apparent perception of whether a phenomenon (e.g., exposure to the incident radiation) has altered the visual appearance or has weakened the structure of the analyzed object. The day-to-day division of experiments into the categories of "destructive" and "non-destructive" by museum scientists is usually based on this definition of damage. Visual observation by the naked eye, strain testing, stereomicroscopes and light microscopes under a variety of illumination is standard practice in the conservation and archaeological fields as a first level of inspection [21-23]. Professionals in the field have often developed an exceptional skill for observing even minor changes to the analyzed material. Color change (e.g., reflectance, absorption, and scattering) provides indirect confirmation of the alteration of physical properties of materials, and is a sensitive probe of material transformation (e.g., structure of crystalline compounds, chemical bonding, oxidation state, and morphology) [24] For example, alteration upon irradiation may lead to the visible formation of color centers in modern glasses, historical pigments or paleontological teeth [25–27], or to the browning of organic compounds [28–30] (Fig. 1).



Fig. 1. Impact of electron-induced damage on synchrotron photoluminescence characterization. (a, b) The sample is maple wood with two layers: (bottom layer) hide glue, deposited from a 20% solution in water, and (upper layer), sandarac resin deposited from a 20% solution in ethanol 96%. The sample was deposited on the rear of a TEM grid that protected some areas from irradiation. (c, d) SEM examination was performed at 0.6–0.8 kV on unmasked areas using a 30- μ m aperture. Further EDX maps were produced at partial N₂ pressure (40 Pa) at 15 kV (120- μ m aperture, "unrealistic" 1.5-h exposure). (e–g) Note the impact on the distinct sectors of the sample as seen using light microscopy (e). As seen under light microscopy under UV illumination with a Hg-lamp ($\lambda exc = 450-490$ nm, $\lambda em >515$ nm), when the electron dose increases, the luminescence intensity reaches a maximum (area 1) and then decreases until becoming negligible (f). This can also be observed when collecting synchrotron UV luminescence images ($\lambda exc = 275$ nm, $\lambda em = 500 \pm 10$ nm) (g). [Figure courtesy A. Vichi (IPANEMA) and J.-P. Échard (Musée de la Musique, Paris)].

2.2. ... is not the only radiation-induced side effect

While visual inspection is a useful qualitative guide for many processes, it is not sufficient to denote the presence or absence of many forms of damage, which can modify the analyzed material at atomic and molecular levels. Except in highly transparent media, such as some glasses and polymers, material optical response will indicate changes in properties at the surface or within the first $100 \,\mu m$ in depth, and may not identify bulk modification. Very local alteration due to microprobes or nanoprobes may also not be observable. Damage can alter the molecular structure, or the electrical, optical or magnetic functional response of the material. Visual inspections do not bring reliable information on the type and the quantity of defects created, their time dependence, their mechanism and the reversibility of the structural changes. Indeed, modifications not visible through a first level of inspection, such as changes at atomic and molecular levels that may lead to delayed damage, are usually overlooked. Changes may affect current or future analyses of the sample, such as speciation measurements, dating and DNA amplification [31]. It is therefore important to have knowledge of the prior forms of analysis performed on the sample. In this way, any previous radiation damage can be incorporated into an understanding of how the material will respond to later analysis in order to adapt experimental procedures.

Observing beam-induced changes between two states of a material is an experiment in itself. As for any characterization of cultural heritage materials, specific difficulties may arise from the spatial heterogeneity of the materials involved, their occasional local chemical metastability, the rarity of materials, the difficulty in modeling them and finally lack of prior knowledge. Damage is inherent in all forms of analysis and in everyday exposure and handling. However, in most cases of cultural heritage research, any alteration is seen as a negative evolution along the path that ultimately leads to artifact destruction and disappearance. In addition, in some cases, a "non-destructive" technique could inherently induce more damage than a "destructive" technique. In the case of a destructive technique, the amount and the location of the sample consumed during the experiment can easily be determined. There is currently no easy way to evaluate the damage to specimens when using "nondestructive" techniques. There is therefore a need and a curatorial demand to improve assessment of the extent of damage that occurs during any experiment. Using a "minimally-destructive" technique in conjunction with information-rich technology is usually the common strategy for increasing the ratio of information collected to radiation damage for high-risk experiments.

Recent advances in analytical techniques facilitate the study of experimental conditions and fundamental factors that lead to alteration of specimens. Indeed, to gain better insight, alteration to the sample should first be measurable. For example, minute quantities of damage to biological macromolecules in the form of oxidation, deamidation, racemization, isomerization and truncation can now be detected using capillary electrophoresis and ultrahigh-pressure nano liquid chromatography in conjunction with hybrid mass spectrometry (MS) [32]. The detection of minor changes in the oxidation state and local chemical environment can also be done using photonic vibrational and speciation-probing approaches across the electromagnetic spectrum [8,33] and electron microscopy with TEM-EELS [34]. New imaging capabilities using SR, laser and IBA techniques allow the sensitive study of minute variations in composition, molecular and chemical environment, structure and morphology at the μm or sub- μm scale. The complex behavior laws involved in material modification can be studied by analyzing materials jointly at the successive characteristic length scales involved (e.g., over three orders of magnitude in length scales of 0.1-100 µm) [35]. Development in correlation of local studies at the molecular level along with imaging capabilities therefore appears

critical for effectively assessing the heterogeneity of damage within cultural heritage materials.

In the rest of this review, we retain the term "damage" when alteration can be observed visually, while we use "radiation-induced side effect" (or, in brief, "radiation side effect") for all other cases.

3. Brief review of radiation side effects on ancient materials

3.1. Historical perspective

We presume that the history of the observation of radiation side effects follows that of the use of analytical techniques based on intense radiation sources. However, reports are scarce and primarily contained in the grey literature rather than more widely available written sources, such as articles and books.

The first analytical methods used in archeometry and heritage were invasive [optical emission spectroscopy (OES) in the 1920s– 1930s] or implied large beam footprints and/or deep penetration [X-ray radiography, and neutron activation analysis (NAA), both first used in the field in the 1950s] [36]. In both cases, being invasive and destructive or low-dose, alteration upon irradiation of samples was not identified as a major issue and was considered low priority compared to the race to smaller sampling volumes and higher spatial resolution. An exception was NAA, all the more so because the elemental composition of heterogeneous materials (hence their activation behavior) is not easily predictable.

After these seminal developments, a main objective was to increase the sensitivity of methods to traces {e.g., how the question of provenance was raised and tentatively addressed in archeometry, as reported by Pollard et al. [37]}. The development of ion beam analysis (IBA) techniques, namely Rutherford backscattering spectrometry (RBS) and nuclear reaction analysis (NRA), dates back to 1957. The field of applications rapidly expanded in the early 1960s, mostly thanks to the development of semiconductor detectors. Accelerators entirely devoted to IBA were built all around the world. Another IBA method, proton-induced X-ray emission (PIXE), was developed in 1970. International conferences on this new field were soon held – IBA in 1973 and PIXE in 1977. Applications to art history and archaeology were initiated in 1972 and grew rapidly because of the intrinsic capabilities of these new tools [5,38]. PIXE, electron microscopy and Castaing microprobe examination led to the first intense irradiation of microsamples causing significant radiationinduced effects.

Soon after the discovery of the laser, derived analytical techniques were proposed in the context of archeometry and art conservation. Early reports described the use of laser microspectral analysis (a combination of pulsed LA sampling with spark-induced optical emission spectrometry) in the determination of the elemental content of metal, pottery and paint samples from different objects [39,40]. In the 1990s, laser-induced breakdown spectroscopy (LIBS) was shown to be a versatile technique for quick, surface elemental analysis on samples as well as on heritage objects [41]. The introduction of Raman microscopy by Delhaye and Dhamelincourt in 1975, and the development of portable spectrometers have revolutionized the use of Raman spectroscopy in art diagnostics and archeometry [16,17,42-46]. Similarly, laser-based fluorescence techniques have been used for the spectroscopic analysis, imaging and lifetime imaging, and multi-photon fluorescence microscopy of cultural heritage materials [15,47–50]. Laboratory X-ray radiography, medical X-ray scanners, and color-controlled UV photography on large-to-medium-scale installation were also strongly developed throughout the 1970s and 1980s in cultural heritage [51].

The trend to decrease X-ray, ion and electron beam sizes for micro and nano focused imaging made the topic of radiation-induced side effects more pressing (Table 1). For example, the development of

Table 1

Typical estimated surface dose rates during synchrotron characterization of cultural heritage materials. Note that, at high incident energy, the surface dose is lower, as it is distributed in a thicker volume. (BM, Bending magnet)

Experiment	Energy hv, keV	Beam size s, μm²	Flux n, ph/s	Estimated surface dose rate D, MGy/s
Post-edge XAS at the iron K-edge on pure goethite (BM)	7.2	3 × 3	1×10^9	3.3
SAXS on an archaeological hair sample	12.7	1×1	1×10^{11}	1.2×10^{2}
Multielemental XRF analysis of an otolith sample (BM)	17.5	3×3	1×10^9	$1.0 imes 10^{-1}$
μCT on a compact bone	30	2000×2000	1×10^{12}	1.1×10^{-4}
µSTXM on a typical proteinaceous material	0.285	0.1 imes 0.1	1×10^9	$1.3 imes 10^4$
µXRD study of lead chromate samples	18	1.6 imes 0.6	$7 imes 10^{10}$	1.6×10^{3}
Speciation imaging of lead chromate samples at the Cr K-edge	5.96	0.66 imes 0.18	$5.9 imes 10^8$	$1.8 imes 10^2$

Surface dose rates are calculated as $D = nh\nu\mu/(s\varrho)$, where *n* is the photon flux, *h* ν the incident photon energy, μ the sum of the atomic photoabsorption and inelastic scattering cross sections as calculated using [52], *s* the beam footprint area and ϱ the material density.

low-aberration lenses for focusing ion and electron beams in the 1990s, and of undulator-based third-generation synchrotron sources in the same period, led to increases of 3-4 orders of magnitude of the flux in the analysis spots of corresponding microbeams. Historically first used as a complement to PIXE, and tested as a potential replacement, synchrotron XRF was introduced in the late 1990s [53,54]. Synchrotron speciation-based methods were introduced in cultural heritage in 1995 [55], IR spectroscopy in 2003 [56], 3DµCT followed only in the mid-2000s [11] and UV/visible spectroscopy and imaging as late as 2011 [9,57]. A current trend is fast synchrotron XRF scanning of entire paintings and heritage samples, leading to more systematic characterization of objects [58,59]. The first International Conference on Synchrotron Radiation and Neutrons in Art and Archaeology was held in 2005. The development and the standardization of exposure of sensitive samples to micro-X-ray beams in other fields of research, in particular biocrystallography, led to the implementation of specific procedures, such as the use of cryostreams [60].

Similarly, reports are scarce concerning damage induced during laser irradiation of samples. In general, laser diagnostic techniques based on spectroscopic or optical coherence methods are considered totally non-destructive. This is largely correct, considering that the laser-beam power density is maintained at very low levels in this type of measurement ($<10^{-3}$ W·mm⁻²). However, thermal or photochemical effects may arise as a result of prolonged irradiation when highly absorbing or photosensitive materials are examined, particularly under focused beam conditions¹. Interesting works were published on the laser-ablative cleaning of heritage objects, which focused on side effects of the overall ablation process on the treated object or artwork {e.g., discoloration of pigments [61], stone surfaces [62], and free radical-induced degradation of binders or paper [63–65]}.

While almost never described in scientific papers, basic precautionary measures were implemented for all corresponding instruments with the aim of minimizing the impact of beaminduced alteration of samples. However, the current evolution of techniques and practice brings new problems. Novel strategies of digitization imply the study of entire objects (e.g., large-scale radiography and UV photography, scanning XRF or PIXE imaging of entire artifacts or paintings, and 3D tomography of fossil collections). Miniaturized high-intensity X-ray and laser sources are becoming available for investigation on site or directly in a museum environment to avoid transportation of fragile artifacts or to provide immediate diagnosis. Micro-characterization methods using intense radiation sources have steadily developed at large-scale facilities and in the laboratory environment.

3.2. Effects reported on the main classes of cultural heritage materials

Radiation effects from ions, electrons, photons can affect material properties, including chemical, electrical, magnetic, mechanical and optical properties. Only a surprisingly small number of review articles detail the impacts of radiation damage during the study of cultural heritage materials {e.g., IBA [5,66,67] or neutron autoradiography [68]}. No equivalent review was identified for SR or laser characterizations (Raman spectroscopy, LIF). This section therefore provides an overview on typical radiation effects for the distinct classes of cultural heritage materials.

3.2.1. Composite materials

Many cultural heritage objects consist of complex composite materials. Examples include paints, which are mixtures of (often inorganic) pigments in organic binders, and biomaterials, such as parchment and paper, which have surface and diffusion layers of ink and sizing agents inside their organic matrix. The interaction between different compounds can be complex. Often their radiation sensitivity, mechanical properties and absorption coefficients are very different. For example, intense radiation can heat a strongly absorbing pigment, which can lead to mechanical damage (e.g., cracking) in the binder. Secondary radiation effects produced by strongly absorbing particles can enhance the degradation of an inorganic matrix. However, indirect radiation effects from activated solvent species or from moisture can lead to corrosion of pigments and other reactions. It is important to note that most cultural heritage materials are impure and can therefore display complex behavior. Natural materials are hierarchically structured, consisting of very different types of materials on mesoscopic length scales [e.g., hard inorganic crystallites in organic matrices (bone, and shells) or alternating domains of high crystalline order and amorphous material (silk, wool, and hair)]. However, integrated studies of radiationinduced damage, taking fully into account the composite nature of such materials, have not been reported so far in cultural heritage contexts, probably due to the difficulty of disentangling the intricate mechanisms involved. More literature has therefore been produced on simpler systems.

3.2.2. Metals and corrosion layers

Metals are among the most radiation-resistant materials. Their high thermal and electrical conductivity reduces the impact of heating and charging effects arising from beams. Prolonged exposure to radiation can accelerate oxidation and corrosion, especially in the presence of water and oxygen (see "indirect effects"). While

¹ Laser sampling analytical methods, such as laser-induced breakdown spectroscopy (LIBS) and MS-based imaging, are not considered in this review as they are based on laser ablation and lead to distinct classes of questions regarding damage and to significantly distinct mitigation and monitoring strategies.

20.02

photon radiation hardly affects metals, ion beams can displace or change the sample atoms, reducing strength and ductility. Strong exposure leads to cracks, changes of the crystallographic structure, amorphization or deformation. However, the effect of radiation on metals contained within cultural heritage materials is still an area where investigation has been limited.

Many of the metal artifacts of interest are heavily corroded [e.g., due to long-term ageing between deposition and recovery (archaeological artifacts), or impact of the outdoor environment (built heritage)]. Compounds in corrosion layers of metals are often far more sensitive to radiation-induced effects than pure metals or alloys. For example, Monnier et al. identified artifactual S⁴⁺ species (2478 eV) resulting from irradiation while performing XANES at the S K-edge on corrosion layers from the iron chain of the medieval Cathedral of Amiens [69]. Sulfur was most probably deposited in cracks from atmospheric pollutants.

Detecting radiation-induced changes is particularly important, as metastable compounds may play leading roles in long-term corrosion mechanisms of metal artifacts, as suspected, e.g., for iron hydroxychloride β -Fe₂(OH)₃Cl [70].

3.2.3. Minerals from gems, ceramics and pigments

The structure of such materials is generally resistant to radiation effects. However, their heat and electrical conductivity are often much lower than those of metals, which leaves them vulnerable to thermal effects of high-power beams. Ionizing radiation may induce color changes through electrical effects (e.g., speciation changes), and alter optical properties that are often very important to the cultural heritage objects to which they belong (e.g., gems and pigments). Also, exposure to charged particles can lead to mechanical weakening of the sample, as described for metals. Thermoluminescencedating measurements, widely used on ceramics, may also be corrupted by analytical radiation.

Absil et al. [25] reported the study of dark brownish stains that appeared on pigments during irradiation with 2–3 MeV protons for PIXE analysis. The study aimed to understand the physical processes of the stain formation and to find ways to make stains disappear, avoiding any damage to the painting. A variety of characterization techniques were used including electron paramagnetic resonance (EPR) spectroscopy, Raman spectroscopy and thermoluminescence. The phenomenon was found to be reversible and not due to molecular changes. These stains progressively faded after a few weeks. Stains also appeared in vacuum, so it was concluded that air does not play a role in their formation. Heat and UV light were found to be the most powerful ways to decrease the stains. It was concluded that the stains were observed only on samples containing carbonates and may have resulted from to color centers induced in the crystal lattice.

The darkening of pigments is occasionally observed in Raman or fluorescence microscopy, such as, for example, the conversion from goethite [yellow ochre, FeO(OH)] to hematite [red ochre or Mars red, Fe_2O_3] upon irradiation by lasers [71]:

$$2 \operatorname{FeO}(OH) \xrightarrow{h_{\nu}} \operatorname{Fe}_2 O_3 + H_2 O \tag{1}$$

In the context of the study of iron-oxide pigments from wall paintings in Knossos (Crete, Greece), model samples of goethite were irradiated at 5 mW ($20\times$ objective, 10 s, $50 \,\mu\text{m}$ diameter, Fig. 2). Under these conditions, only features from hematite were observed, thereby confirming the full conversion. Local modification of the color of the pigment was observed. At 10 times less power (0.5 mW), only features from goethite were observed. Such effects can be "reversible": the partial darkening of lead white paint was seemingly reversed, in relation to laser cleaning or LIBS analysis [61,72].



Fig. 2. (a) Raman spectra of a yellow ochre (goethite, FeO(OH)) model sample collected under low-power (i) and high-power (ii) irradiation conditions and of a red ochre (hematite, Fe₂O₃) sample collected under high-power (iii) irradiation conditions ($\lambda exc = 786$ nm, 20× objective). (b, c) Images of the yellow ochre sample before (b) and after (c) high-power irradiation, respectively. The darkened area after irradiation (diameter: 40 µm) is considerably greater than the irradiated area (beam size: 5 µm). Scale bar is 20 µm. [Figure courtesy A. Philippidis (IESL-FORTH)]

Another example is the fading of artists' pigment Prussian blue under intense light or anoxia, due to reduction of Fe^{III}:

$$KFe^{III}[Fe^{II}(CN)_{6}] \xrightarrow{+K^{+}, e^{-}} K_{2}Fe^{II}[Fe^{II}(CN)_{6}]$$
(2)

This leads to pigment discoloration, as the dark blue color of Prussian blue results from intervalence charge transfer between the two iron sites of this mixed-valence compound (Fe^{III}, Fe^{III}). X-ray irradiation while performing X-ray absorption spectroscopy (in anoxia) leads to a shift of the Fe absorption edge that is primarily attributed to beam effects (Fig. 3) [73].



Fig. 3. *In-situ* Fe K-edge XANES successive spectra on Prussian blue-dyed paper under anoxia and visible light illumination $(1.5 \times 10^6 \text{ lux})$. The shift of the energy of the absorption edge is attributed to the reduction of Fe(III) to Fe(II) induced by the beam. The structural evolutions can be studied in terms of fading induced by X-ray irradiation. [Figure courtesy M.-A. Languille (IPANEMA) and Cl. Gervais (Bern University of the Arts, Switzerland)][73,74].

As part of a study on the durability of several types of chromevellow pigments, pure lead chromate (both in monoclinic and orthorhombic form) and several monoclinic co-precipitates of PbCrO₄ and $PbSO_4$ ($PbCr_{0.76}S_{0.24}O_4$ and $PbCr_{0.54}S_{0.46}O_4$) were synthesized [75]. These materials were irradiated with an 18-keV monochromatic X-ray beam of $\sim 7 \times 10^{10}$ photons per second (ph/s) during a series of 100 intervals of 10 s at the P06 X-ray microprobe beamline of PETRA-III. The beam was focused to dimensions of $0.6 \times 1.6 \,\mu\text{m}^2$. After each interval, an XRPD image was recorded. The observed diffraction lines gradually reduced in intensity, indicating a progressive amorphization of the material (Fig. 4b,c). The higher the sulfate content of the chrome yellow, the quicker this beam-induced degradation progressed inside the three monoclinic materials (Fig. 4d); the loss of structure in the orthorhombic PbCrO₄ was even faster (Fig. 4e) and initially appeared to follow second-order kinetics. Since significant changes occurred within a time scale of 10 s or more, this phenomenon did not impede the recording of XRF/XRPD maps with typical dwell times of 0.5-2 s, although it could impact on data collection that takes longer (e.g., X-ray absorption spectroscopy).

3.2.4. Glasses

Glasses behave very similarly to other minerals, generally having low heat and electrical conductivity. Glasses in cultural heritage objects almost always contain additives to engineer their optical properties, and impurities from the raw material and the fabrication process. These can lead to rapid formation of color centers, which cause discoloration or darkening of the glass and can have a strong visual impact due to the transparency of glass in the visible.

3.2.5. Organics, including polymer films and fibers, oils, varnishes and dyes

Organic materials are much more sensitive to the effects of ionizing radiation than inorganic materials. Focused beam conditions can lead to melting. Organic bonds are easily broken by primary and secondary radiation effects. The excited molecules (charged or radical-bearing) quickly form new chemical bonds leading to crosslinking, aggregation, decomposition, oxidation and isomerization. These effects can structurally weaken a polymer by making it brittle, causing its discoloration or decreasing its solubility and change its spectroscopic response (Fig. 1). Within the context of cultural heritage artifacts, the optical properties are often very important (e.g., oils, varnishes, and dyes). Above certain thresholds, discoloration and decomposition can lead to visible marks left by the analyzing beam. In addition, indirect effects from the matrix or solvent can strongly accelerate degradation.

The photochemical stability of organic coatings and films has been studied in the context of research on the impact of radical formation during laser-ablative cleaning of varnished paintings. Thin films of PMMA (Poly(methyl methacrylate)) or polystyrene simulating varnishes with low and high absorbance in the UV, were doped with photolabile organic molecules (e.g., aryl iodides), followed by irradiation at 248 nm with ns and fs laser pulses [63,76]. Photocleavage of the weak Ar-I bonds resulted in the formation of Ar radicals, which formed highly fluorescent arenes via H abstraction that served as sensitive fluorescence indicators of photochemical activity in the organic film as a function of laser-irradiation dose. The doped film concept could serve as a



Fig. 4. Synchrotron microdiffraction study of the darkening of yellow lead chromates. (a) Sample showing the darkened irradiated spot when performing synchrotron μ XRD (18 keV, 7×10^{13} ph/s, $1.6 \times 0.6 \ \mu$ m²). The deposited dose is estimated at 1.6×10^3 MGy/s. (b,c) Change over time of the X-ray diffraction pattern of monoclinic PbCrO₄. (d,e) Evolution over time of the intensity of XRD features of distinct lead chromates. Note that the reported alteration happens on a time scale of hundreds of seconds, far beyond usual data collection times at synchrotrons, in the 0.1–1 s range.

sensitive, straightforward sensor to investigate photochemical effects of synchrotron or ion beams on organic media. The literature on testing macrofading and microfading, used to establish safe-lighting conditions in museums, also constitutes a source of information on irradiation behavior under the near-UV and the visible [77].

Radiation stability of organic materials (e.g., Mylar foil, Kapton foil, PDMS (Polydimethylsiloxane) and Fe(III)TPP) (Tetraphenylporphyrin) were investigated with focused 1600 keV He+ ion beams. Area-selective irradiation or damaging were carried out with simultaneous H-count-rate measurements as a function of the deposited ion-beam fluence within the range 10¹⁴–10¹⁵ ions/cm² [78]. The results show that both the Kapton foil and the Fe(III)TPP complex did not suffer from hydrogen depletion while there was a slight decrease of the hydrogen content of the Mylar foil and a remarkable exponential loss of hydrogen from PDMS, suggesting degradation of the polymer chain. Hydrogen loss takes place by an irreversible process of homolytic scission of C-H bonds. It is well known that molecules containing aromatic functional groups are generally more stable under irradiation. However, Mylar contains aromatic groups that provide relatively high radiation stability but also ethylene groups, which can undergo bond scission to result in some H loss. The Kapton polymer and Fe(III)TPP molecule contain almost only aromatic bonds, so they have high radiation stability. By contrast, PDMS, with only single covalent bonds, has low radiation stability.

3.2.6. Organo-metallics, soaps, lakes and inks

Organo-metallic compounds, soaps, lakes, and inks are known to be sensitive to beam damage. While studying the Fe^{2+}/Fe^{3+} ratio of iron-gall ink manuscripts, Kanngiesser et al. and Wilke et al. both reported a shift to lower energies with radiation exposure time of the Fe K absorption edge, as revealed by a time series of XANES spectra collected at the same position. This is indicative of a reduction of the Fe^{3+} ions to Fe^{2+} with radiation dose, while the organic matrix acts as an electron donor [79,80].

Mazel et al. observed a similar photoreduction of iron under an X-ray beam during XANES investigation of blood remains from the patina of Dogon anthropomorphic statuettes [81]. They note that "for the area where mineral compounds are supposed to be predominant, this evolution is not observed", using radiation damage as further demonstration of the presence of iron atoms in an organic environment.

3.2.7. Unmineralized biomaterials, including wood, textiles, parchment, paper, leather

This large group of cultural heritage materials is arguably the most radiation sensitive and great care has to be taken in conducting irradiation experiments [30]. In addition to the above points regarding polymers, biological materials very often contain significant amounts of water, which leads to indirect radiation effects. However, removing the water from the sample can result in even greater morphological damage. Biological materials are prone to aging by radiation. Mechanisms of aging include racemization, deamidation, oxidation, and truncation (Fig. 5) [82]. Modern technologies enable us to gain deeper information about biomaterials by studying subtle changes in their molecular structure.

Sandström et al. reported a limited reduction of the sulfate signal (SO₄⁻²/HSO₄⁻; 2482.6 eV) *versus* an increase of the elemental sulfur (2473.0 eV) while studying waterlogged wood from ancient ship-wrecks after long exposure [83].

Moini et al. examined the effects of various ageing techniques on aspartic-acid racemization in silk samples. Modern silk specimens were exposed to UV-lamp radiation for 200–1920 h with a resulting increase of the D/L ratio for aspartic acid from 5.4% to 8.8%. Untreated modern silk exposed to electron-beam radiation showed an increase in the D/L ratio of aspartic acid from 3.3% to 5.7% (Fig. 6) [84]. Recently, similar results were also reported on the effect of synchrotron X-ray irradiation on proteinaceous specimens [85].

Published examples highlight that the lack of understanding of the basic radiation-induced damage mechanisms may lead to unexpected response of materials during analysis. For example, PIXE analysis of manuscripts resulted in visible damage being manifest only months later [28]. Mantler et al. made an in-depth study of X-ray-induced paper degradation under varying irradiation conditions (exposure time, voltage and intensity of the rhodium tube, and aluminum filters) and concluded that the collection of data in conditions required by wavelength dispersive XRF spectroscopy may lead to "permanent yellowing, brittleness, and even mechanical decomposition" of paper [86].

Patten et al. studied the changes in parchment samples after exposure to an X-ray dose during high-contrast X-ray microtomography and used a series of analytical methods to check for alterations (i.e. ATR-FTIR, biochemical analyses, near-IR analysis, and XRD). They could not find evidence of any change but such an experiment would surely be interesting to repeat with a source of greater brightness, such as a synchrotron [87].

3.2.8. Biominerals from bone, tooth and fossil tissues

This subgroup of samples is generally very radiation hard and suffers little visible damage during irradiation. Color changes are often observed in the irradiation of teeth and similar materials. Most importantly, however, fossils might still carry traces of their original organic content (e.g., DNA, and proteins), which, unlike the bulk mineral, could be highly radiation sensitive.

Richards et al. studied the blackening of modern and fossil teeth under X-ray µCT [27]. By irradiating bands on teeth using synchrotron X-rays under realistic experimental conditions, they compared the blackening observed with varying irradiation durations, X-ray photon energies, origins and history of the samples of teeth. They further studied how colored tooth enamel could be bleached using exposure to UV light, and observed occasional remains of darkening.

Contrasting results were published regarding the impact of X-ray irradiation on the DNA-amplification potential from archaeological bones [31,88]. Irradiated bones where analyzed using polymerase-chain-reaction amplification methods to assess the impact of CT experiments on the preservation of DNA.

3.3. Complementary sources of information

The above review shows that the literature on radiation damage affecting cultural heritage materials is limited and patchy, and does not provide a sufficient framework to account for the situations observed. Fortunately, radiation-induced damage is well studied in related fields of research, such as ion implantation for the microelectronics industry, fundamental photophysics and photochemistry, radiobiology on living organisms, biocrystallography (relating radiation damage to XRD reflection intensity and subsequent reconstruction of the electron density), environmental sciences (speciation of trace elements in clay-based materials), and some fields of materials science. References are given in Table 2.

For example, Raman and FT-IR analyses showed that UV light at 248 nm from a nanosecond KrF excimer laser is capable of inducing conformational changes in an irradiated collagen film, mainly as a result of breaking the hydrogen-bond network and loss of water molecules that maintain the ordered structure [114]. In addition fluorescence measurements showed that UV laser light is capable of causing tyrosine photo-oxidation [114]. The effect of X-rays on proteins was studied [115,116] and a study of which amino acids are most affected by synchrotron X-ray radiation was conducted [117]. There are examples of the effect of gamma radiation on the mechanical properties and the solubility of silk and other proteins [118]. Wien et al. described VUV-irradiation effects on proteins in high-flux synchrotron radiation circular dichroism spectroscopy [119].

Radiation effects have been investigated in diverse fields, such as materials science, where material properties can be modified by irradiation. This includes photolithography in the semiconductor industry, space science (where the damage of cosmic radiation to space equipment was investigated) [120], astrobiology and radiationbiology [121] (where the effects of radiation on living organisms are of interest to understand whether life is possible in highlyirradiated habitats such as the surface of Mars) [122], and military applications (e.g., anti-missile systems based on high-power lasers). However, a limited number of systematic studies have been performed on radiation damage that occurs as a side effect of analytical and irradiation investigations.

Soft X-rays are increasingly being used to study the speciation of carbon and nitrogen in wet organic samples in the so-called "water window" [99,123] or in other materials. Examples in cultural heritage include the study of the L absorption edges of transition metals [124]. In the low-energy X-ray range, the dose deposited may reach extreme values, due to the large cross-section of elements and has led to accurate comparisons between radiation damage under photon speciation (STXM), electron speciation (TEM-EELS) and X-ray diffraction microscopy [109,125,126]. In particular, Howells et al. showed that there is approximately a "linear relationship between the maximum allowed dose and the resolution, with the allowed dose being equal to 1.0×10^8 Gray per nanometer of resolution" and discussed practical procedures to estimate thresholds [126].

As a result of standardized experimental set-ups and data analysis in synchrotron protein crystallography, experimental conditions leading to minimal damage could be defined more clearly than in other fields [92–94]. In crystallography, radiation damage can be monitored from the loss of long-range order that leads to broadening or vanishing of Bragg peaks during the experiment (Table 2). This allows quantification of damage and enables researchers to measure directly the effects of mitigation strategies (e.g., cryocooling).

However, many other aspects of radiation-induced damage that have not been studied are likely to have a strong impact on cultural heritage research, e.g.:

- the mechanisms of degradation of proteins used as binding media in heritage varnishes and paint layers;
- the effects of additives in polymers;
- the deterioration of radiation-sensitive pigments, such as mixedvalence inorganic compounds; and,
- the effects of trace-elemental concentration and crystal defects on the damage induced in ancient materials, such as teeth, glass.

In the following section, we present a brief account of how each relevant form of radiation interacts with matter and what forms of modification are produced in different classes of cultural heritage materials.



Fig. 5. Mechanisms leading to alteration of organic materials under ionizing radiation.



Fig. 6. (a) Effect of UV radiation on silk aging. Average D/L ratios for silk samples treated with UV radiation for 0, 348 h, 596 h, 1280 h and 1920 h. The inset shows the electropherograms for the samples treated with UV radiation for 0, 596 h and 1920 h, focusing on the aspartic acid D and L peaks (547 *m/z*), along with 16 × magnification of the D peak. [Reproduced with permission from ACS [82]]. (b) Effects of ozone, electron beam, and chlorine exposure on silk aspartic acid racemization.

Table 2

Fields of research that may allow significant transfer of information to cultural heritage with respect to radiation-induced effects

Scientific field	Торіс	Ref.
Life sciences	Radiobiology Impact of radiation on living organisms	[89–91]
	Radiation damage to protein crystals studied in molecular crystallography Damage to active sites in	[92-96]
	metalloenzymes	[,]
	NEXAFS / STXM synchrotron-based studies of biological cross-sections	[99]
Environmental sciences	Radiation effects on the speciation of trace elements in soils and clay-like materials	[100]
Material sciences (Hard condensed matter)	Damage to crystalline materials Radiation-controlled material synthesis and engineering	[7,67]
	Photonics Space science	[101,102]
	Radiation hardness of semiconductors and core materials	[26,103,104]
	Damage to X-ray optics	[105,106]
	Lithography, ion implantation and doping	[107,108]
Material sciences (Soft condensed matter)	Radiation damage to polymers and plastics	[78,109–113]
Fundamentals of radiation damage	lon-induced radiation damage lon/solid interactions Fundamental photophysics	[1,6,7,67]

4. Basic mechanisms of interaction between probing particles and matter

Cultural heritage objects and samples are exposed to charged particles, photons and neutrons to create interactions as a basis for analysis. The radiation used is not necessarily harmful to the material but there is usually a limit above which it causes visible damage. In order to determine the specific radiation effects and thresholds for visible damage to a cultural heritage object, one needs to consider the type of radiation used and its interaction mechanisms with the material under analysis.

4.1. Primary versus secondary radiation effects

The following conventional definitions are used (Table 3; Fig. 7):

• *Primary* radiation effects result from the interaction of an incident particle (e.g., an ion or a photon) with a target atom or molecule.

Table 3

Examples, for the case of X-rays, illustrating the definition of direct, indirect, primary and secondary irradiation effects

	Primary effect	Secondary effect
Direct effect	Photoelectric effect in a target atom, creating an ion and a fast electron.	Inelastic scattering of the photoelectron, creating electron cascades and more ionization.
Indirect effect	Photoelectric effect in a solvent molecule, creating a reactive species (<i>e.g.</i> formation of OH radicals).	Chemical damage to the target molecule by the reactive species.



Fig. 7. The different types of radiation effects in a sample in an (aqueous) environment. Primary radiation effects (yellow star) are caused by interaction of an incident particle (shown in red) with a sample atom or molecule (shown in grey). The interaction can result in secondary particles, such as photoelectrons, being emitted (shown in light blue). Secondary particles can themselves interact with neighboring atoms for secondary radiation effects (green star). Indirect effects are caused by interaction of incident particles with the solvent (orange star), creating aggressive species (shown in green), which can themselves react with the sample (red star).

- Secondary radiation effects result from the interaction of a secondary particle, for example a photoelectron or a displaced nucleus, with a target molecule or atom.
- If this primary or secondary interaction happens in a target atom or molecule, the effect is *direct*.
- Indirect effects contain all possible reactions when an atom or a molecule of the solvent, environment, host matrix, or substrate is hit, creating a chemically reactive species that reacts with the target atom or molecule. Typical examples of indirect effects are reactions with water radicals and solvated electrons resulting from radiolysis of aqueous solvents [127].

4.2. Impact of experimental parameters on radiation-induced effects

This section discusses and defines the most important experimental and environmental parameters and their influence on radiation-induced effects.

4.2.1. Probing-beam parameters

Flux (or intensity) is the number of particles (e.g., photons or ions) that travel through a unit area per unit time. Lasers produce very high fluxes, as do, to a lesser extent, focused synchrotron beams. Thermal and charging radiation effects are flux dependent, as they depend on the ratio between the rate at which energy or charge is deposited or generated, and the ability of the sample and environment to dissipate it. High fluxes can also lead to molecular interactions, when radicals are created fast enough to interact with each other instead of reacting with their environment. The products of these interactions can open new reaction pathways. The energy of the incident particles (not to be confused with the flux or deposited dose) depends on machine parameters (e.g., the acceleration voltage for ion beams, or undulator, filter and monochromator parameters for synchrotron beams). Many channels of radiation effects are activated at certain particle energies (e.g., ionization energy). Spectroscopy experiments that are bound to these energy thresholds, such as XAS and UV photoluminescence spectroscopy, leave no possibility to optimize the energy parameter except to change conditions dramatically by switching, e.g., from K- to L-shell transitions. In addition, for ion beams and X-rays, the penetration depth is strongly energy dependent. For soft-to-medium X-rays, the penetration depth will typically vary as E^3 . Lower energy beams will thus deposit most of their dose at the surface of the sample, while higher energy particles will distribute the energy in deeper layers (Table 1). Depending on the method used, there can be optimal energies, where the signal-to-damage ratio is highest. The detector efficiency, which is often energy dependent, has to be taken into account.

Fluence is the beam flux integrated over time, equal to the total number of particles that have passed through a unit area. In synchrotron experiments, dose is more commonly used, and is a measure of the total (integrated) energy deposited per unit of sample volume. However, both measure the total deposited radiation in a sample area and can be discussed together.

4.2.2. Environmental parameters

High sample temperature can damage the sample and accelerate the kinetics of degradation reactions. However, high temperatures might also have an annealing effect on some materials, allowing crystal defects, such as color centers in glasses to "heal". Cooling the sample can reduce damaging reactions; this is especially true for indirect radiation effects that rely on chemical reactions and diffusion of radicals {e.g. [92]}. However, to achieve a measurable effect, cryogenic cooling is required, and can itself be very damaging to samples. In addition, the damage is not avoided, but delayed. The created radicals will start damaging the sample as soon as the temperature is raised and radicals become mobile.

The sample atmosphere is important, mainly through thermal conductivity, humidity and oxygen concentration. Thermal conductivity mitigates heating effects from high-flux sources, such as lasers. Thermal effects will be more damaging when working in vacuum. Water molecules in the air and in materials will participate in damaging the sample through indirect effects. It is therefore better to work in dry atmospheres. However, many samples, especially of biological origin, do not tolerate low humidity. The oxygen in the atmosphere can degrade the sample though indirect effects, such as ozone generation. In addition, it might oxidize the irradiated parts of the sample. For these reasons, it is generally preferable to remove oxygen during the experiment, by placing the sample in an inert gas atmosphere or by blowing inert gas on the irradiated part. Some compounds, in particular dyes, can reduce spontaneously under anoxic conditions, with charge compensation from the substrate on which they are deposited [73]. Eventually, water molecules inside the sample will contribute to indirect radiation effects (see sub-section 4.1), which can be more damaging than the direct irradiation effects. In many organic materials (e.g., wood and paper), the level of humidity cannot be arbitrarily reduced without causing structural damage.

Surface contamination and trace-elemental concentration of the sample can contribute to indirect radiation effects by chemical reactions of the contaminant with the sample. It is important to note that irradiation can directly damage the sample material and its contaminants, resulting in further chemical reactions and consequential damages. Radiation effects on the contaminated surface could permanently attach the contaminants to the object by radiation-induced chemical reactions.

4.3. Exposure to charged particles

IBA makes use of various ion-solid interactions [6,7,38,67,128]. For analysis of cultural heritage materials, samples are usually exposed to beams of protons or alpha particles that are accelerated to energies of a few MeV. On passing through matter, these highly energetic charged particles interact with the electrons of the material, causing ionization of the atoms present. Using the terminology introduced previously, such ionizing radiation is therefore called direct. As the range of probing ions is usually a few tens of μ m, a large amount of energy is deposited within this depth. As charged particles traverse through the material, they slow down as they lose kinetic energy. This loss of energy may be divided into two components based on the mechanism of energy transfer, resulting in collisional or radiative energy loss. Energy loss to electrons occurs due to Coulombic interactions (i.e., ionization and excitation), and nuclear energy loss occurs due to emission of Bremsstrahlung or Cerenkov radiation, and nuclear interactions. Initially, an ion mainly loses its energy in small steps via interactions with the electrons in the material through which it passes. Once it no longer possesses sufficient energy to excite an electron, the ion mostly loses its energy by nuclear collisions. As the ion slows down, it captures one or more electrons to form a neutral atom (e.g., a proton forms a hydrogen atom and an alpha particle a helium atom).

Similarly, when high-energy electrons pass through matter, several possible processes occur, including:

- 1 ionization, in which the energy-loss mechanism is similar to that for heavy charged particles;
- 2 Bremsstrahlung, which is the creation of X-rays from electron deceleration; and,
- 3 elastic scattering from nuclear and electronic interactions.

Ion and electron irradiation can result in the following effects to analyzed materials:

- changes in electronic configuration (impurities, color centers, creation of charged species), resulting, e.g., in visible changes in sample color or reflectivity;
- displacement of atoms in the sample, which results in reduced crystallinity;
- the energy deposited by the beam can cause sample heating, resulting in macroscopic softening or distortion of the sample;
- as particles are charged, charges can build up in isolated samples, which can lead to damage due to high-voltage breakdown;
- changes caused in microscopic structures by the creation of structural defects and the formation of new phases; and,
- ions can cause surface roughening due to sputtering and modify the composition of the sample by implantation or nuclear reactions.

4.4. Exposure to photon beams

Unlike ions and electrons, photons are not electrically charged and carry a much smaller momentum. Their interaction with materials can be classified via the following regimes.

4.4.1. High-energy photons

X-ray and γ -ray photons carry enough energy to ionize materials. They can lead to material damage via three effects:

• the photoelectric effect, in which the photon is absorbed and a photoelectron is ejected by the target atom;

- Compton scattering, an inelastic scattering event, during which the photon transfers part of its energy to an electron of the target atom, producing a lower energy photon and a high energy free electron; and,
- at photon energies >1.1 MeV, pair production, in which the photon transforms into an electron-positron pair.

All these processes lead to high-energy primary electrons that release their energy through inelastic scattering in the sample, causing secondary electron cascades.

4.4.2. Photochemical effects (eV-level energy photons, UV/visible)

Photons in this energy range can interact with atoms, molecules or materials, through electronic effects. The absorbed photon energy promotes an electron to a higher energy state (photoexcitation). Depending on the electronic structure of the material, photo-excitation can trigger a large variety of different processes, such as ionization and ion-pair formation, bond dissociation and formation of free radicals, leading to subsequent chemical reactions, including atom abstraction, oxidation, dissociation, crosslinking, and polymerization. Because of their high photon flux, (ns or ps)-pulsed laser sources usually enhance these photochemical effects by temporarily generating a high density of excited states [76].

4.4.3. Thermal effects (low-energy photons, IR)

Photons absorbed deposit their energy inside the material. Depending on photon energy, this energy is dissipated via different relaxation pathways, often including photochemical reactions. However, a large part will activate vibrational or lattice modes of the target and cause heating. Depending on the power of the irradiation source and the thermal conductivity of the sample and its environment, the temperature increase can be substantial, leading to mechanical expansion, deformation of the sample, drying out of humid samples, and boiling of fluids, which can threaten the mechanical integrity of materials (for example, by initiation and propagation of cracks). In addition, heating can cause conformational changes in molecular materials, and accelerate chemical reactions and phase transitions (e.g., such thermal effects may be observed with lasers during materials analysis, particularly when focused beams are used in Raman or laser fluorescence microscopy). Considering spectroscopic techniques, classified as noninvasive, mechanical effects following irradiation are usually minimal and arise mainly because of thermal expansion of the materials.

4.4.4. Specific case of high-power laser irradiation

In the case of high-power laser irradiation, pulsed lasers, typically with pulse duration in the ns-to-fs range, may be used in the LA regime ($P > 10^6$ W·mm⁻²) leading to material removal from the sample surface. LA enables material analysis through a number of schemes {e.g., matrix-assisted laser desorption ionization (MALDI), LA time-of-flight MS (LA-TOF-MS), LA inductively-coupled plasma OES or MS (LA-ICP-OES/MS) and laser-induced breakdown spectroscopy (LIBS) [129,130]}.

In the context of cultural heritage, LA is also used as an advanced cleaning method for object conservation. In LA-based techniques, material removal does take place and is obviously an essential ingredient of the method. This flux regime falls distinctly higher than that described previously (Raman or fluorescence analysis) and working at this regime is always the result of an intentional choice. The rapid transformation of materials from solid to liquid and gas generates significant mechanical stresses [131]. Furthermore, formation of plasma and its expansion against the ambient atmosphere results in the formation of a shockwave that acquires enough energy to cause significant damage to soft materials (e.g., paints). Beyond local ablation, modifications to the remaining

irradiated substrate or sample (around "craters") are observed as a result of a complex interplay of mechanical (stress and shockwave), thermal and chemical effects [61–65].

5. Mitigation strategies

We review below the main approaches implemented to mitigate radiation-induced side effects during the characterization of cultural heritage materials.

5.1. Avoidance of unnecessary beam exposure

Since the extent of material damage directly relates to the irradiation dose, reducing or interrupting beam exposure when data acquisition is not being performed will reduce the risk of sample damage. In order to avoid unnecessary sample irradiation, it is important to select the region of interest (ROI) of the analysis in advance [2]. This is usually done by careful identification of ROIs under an optical microscope, and acquisition of corresponding images. It is very useful if at least one orientation point can be marked on the sample holder and the relative distance of the ROI measured. This way, the sample can be positioned very precisely for measurement in the vacuum chamber or sample holder before analysis. It is beneficial if a high-quality optical microscope is also available for on-line positioning at the instrument. The following measures are similarly recommended:

- pre-alignment of samples rather than in-beam alignment;
- use of control samples to optimize experimental measurement and data collection, which may result in difficulties, as most ancient samples present distinct features at the microscale;
- use of shutters when no data is collected from the sample (requires specific instrumental capacities); and,
- reduction of measurement dead time during irradiation [requires specific instrumental capacities (e.g., optimize continuous scanning) [132,133]].

5.2. Optimization of dose or fluence

Reducing the overall dose arriving at the sample during any analysis is crucial, as most damage types caused by ionizing radiation depend on the dose or fluence. Obviously, this should not result in excessive deterioration of the analytical result. Suggested improvements in experimental set-ups may include the design of more efficient acquisition schemes, leading to enhanced S/N: use of sensitive low-noise detectors; or, detection geometries and detectors that permit signal collection from wider solid angles.

5.3. Optimization of flux

It is also crucial that the flux is optimized to the dynamic range of the detection set-up. Furthermore, a higher flux creates damage faster and makes the experiment more difficult to control. For those types of damage (e.g., thermal effects), which depend on the flux rather than the fluence, a reduction of the flux might reduce the alteration. However, in some conditions, increasing the flux might be beneficial. Considering ionizing radiation, a higher flux will often reduce the interference of indirect effects with the measurement. Suggested improvements in experimental set-ups may include the following:

• Moving the sample or defocusing the beam during acquisition to average out the dose on the sample. This is applicable in the case of homogeneous samples or when spatial resolution at the beam size is not an issue [134–136]. This is standard practice

in PIXE [30]. At synchrotrons, this can also be done by moving the sample out of the focal plane of the excitation beam.

- Keeping the flux at a minimum as long as adequate S/N is maintained, in cases where alteration is flux dependent, which is often true for non-ionizing radiation at optical wavelengths, where thermal effects dominate damage. Examples are laser sources, where minimum power density will keep photochemical and thermal effects to a minimum.
- Considering the optimal size of the area for scanning, together with the pixel size and beam size. For example, in the case of a $1000 \times 1000 \ \mu m^2$ size scan in a 256×256 pixel array, one pixel size is about 4 μm ; working with a smaller beam size might not be worthwhile.
- In most cases, the beam profile will be smooth (e.g., Gaussian or Lorentzian). However, due to imperfect optics it might also have "hot spots", which have a much higher flux. It is important to take these into account because they might cause local flux-dependent effects not expected from the average beam flux.

5.4. Optimization of dwell time

The dwell time is the time the beam stays in one pixel. Fast scanning can reduce the damage by providing more time for energy dissipation. In order to decrease the deposited energy density further, it is possible to use large solid angle detectors [1,137].

5.5. Optimized sample environment and condition

Radiation effects often relate to the sample environment, including its ambient atmosphere or the analyte matrix (see sub-section 4.2.2). The following strategies are used in several laboratories in order to reduce environment-related effects:

- use of a modified atmosphere suitable for the sample (e.g., an inert atmosphere, such as a helium jet, and reduced humidity);
- decreasing the water content within the sample; or,
- lowering the sample temperature.

If heat is not dissipated, it will cause a temperature increase of the sample that could lead to thermal damage. If the analysis is done under vacuum, thermal dissipation is even more limited. Cooling will result in a reduction of diffusive processes in the sample and impede an extensive propagation of ions and radicals. Cryostreams are employed in biocrystallography and soft X-ray imaging of biological cross-sections [92,97]. During IBA, especially with a focused beam [138], the deposited power density can be large (e.g., $800 \text{ mW} \cdot \text{mm}^{-3}$ for a 3 MeV proton beam of $100 \,\mu\text{m}$ diameter at 100 pA current) [30]. Cooling the sample is especially recommended for organic materials. When the measurement is carried out in vacuum, a cold finger connected to a liquid-nitrogen supply can be applied. However, one should note that such a set-up requires a clean high vacuum, as any possible contamination in the vacuum chamber can be frozen to the sample surface. In-air IBA provides better heat dissipation. The cooling is even more efficient, and X-ray absorption in air is minimized, with a helium gas flow in front of the sample.

Each cultural heritage sample is complex, inhomogeneous and impure and will therefore react slightly differently to beam exposure. However, taking into account the guidelines presented in the above section, radiation effects can be minimized and visible damage to the sample can be reduced or even avoided.

6. Monitoring and recording strategies

In addition to mitigation strategies, once a sample is submitted for analysis, different stages of monitoring can be used to characterize its state before, during and after analysis. Each stage must be well documented. Macro or visible damage, micro damage that can be identified with microscopy and, if possible, with molecular or elemental monitoring that requires advanced analytical techniques must be documented. We highlight here a few suggestions that could serve as a basis to produce more general guidelines. Several of these points are usual practice at many facilities while others could be disseminated far more.

6.1. Prior to the experiment

The following steps can be followed.

- 1 Request and document general information about the sample, such as its chemical composition, age, treatment, conservation, and analysis history. In addition, evaluate and document the condition of the specimen, including its appearance through high-resolution or microscopic photography, depending on its size, and document any suspicious feature indicative of prior damage. Macro or visible damage to the naked eye, micro damage that can be identified with optical microscopy, and molecular/ atomic monitoring that requires advance analytical techniques should be documented. Obtaining information about the historical value and the cultural value of the samples is central. Sample handling, therefore, should conform to these values. This sample assessment is comparable to the 'Artifact condition report' done routinely in museums.
- 2 Evaluate the radiation sensitivity of the samples (see Section 4).
- 3 Perform a test run on a control sample, preferably using one as similar as possible in composition to the sample of interest. Use this control sample to optimize the signal while eliminating any damage to it. If a control sample does not exist, evaluate and optimize the impact of radiation on the least visible or an already damaged portion of the sample.

In ideal conditions, the analyst must find ideal measurement parameters at which maximum information is achieved at minimum damage to the sample. Being able to define this threshold in each experiment is largely due to the skill and experience of the analyst.

6.2. During the experiment

When this evaluation part of the analysis is completed, the secondary stage of monitoring takes place during experimentation on the sample. Initially, experimentation must be performed at low dose. Dose should be increased only gradually to attain optimal characterization conditions. At this stage, any unexpected analytical response, such as unusual response or lack of characteristic analyte signal, should be evaluated and documented. Successive measurements must be performed to evaluate changes that appear *in situ*. It is usual practice with many instruments to monitor a selected analytical signal by time to follow possible structural or chemical modifications of the sample (see, e.g., Figs. 3 and 4). S/N is usually constraining here (e.g., readout noise will build up when summing successive images).

Under some analytical conditions, the first measurement may be the best while, in others, it can be the least reliable (sample with contaminated surface in which the first measurement "cleans up" the sample) [139]. In conditions where ablation occurs, the first measurement might remove or add contamination. This result may differ to that obtained from the control measurement due to varied surface history of the samples.

In addition to the reproducibility of successive data, which relates to the condition of the sample, additional and complementary tools, such as optical microscopy, colorimetry, or MS and optical spectroscopy, can be utilized to monitor the condition of the sample for minimal or no damage, depending on the type of experiment being performed. An important evolution would be the advent of "early warning systems" able to alert on the occurrence of radiationinduced side effects during characterization with intense radiation sources. Interestingly, mathematical models were developed for the evaluation of the dose deposited in samples with realistic experimental parameters. For example, Chukalina et al. proposed a procedure to compare the dose deposited during computed and confocal tomography experiments [140]. Information on sampleexposure conditions and location of analyses, and the date and the place of experiment, as well as every important experimental parameter, should be documented [110].

6.3. After the experiment

The last stage of monitoring is an investigation of the state of sample after analysis is completed and its comparison with similar data prior to analysis. Similar to monitoring prior to analysis, post-analysis monitoring includes the same stages. Due to diffusion processes (heat, reactive species), damage can extend far beyond the irradiated area (Fig. 2).

Two types of damage can happen: immediate and delayed. Immediate damage can be identified during the post-monitoring stage, typically after a few minutes delay at maximum. To detect any delayed damage, long-term monitoring is required. The nature and the degree of any damage, including the possibility of long-term damage, should be documented and discussed with curators and conservators, so that they report possible changes in the future, and for assessing impact to future characterization. This will mostly happen during re-examination of the sample. Although rarely done, reports of damage should also be publicly disseminated, including through research articles. It is therefore critically important to document and to preserve all data regarding the effects of the experiments on cultural heritage materials.

7. Conclusion: "Fighting the taboo"

We have reviewed existing works and day-to-day laboratory practice on the effects of intense radiation on cultural heritage materials. This review is a first step in raising awareness, identifying key parameters of the analytical process, and encouraging subsequent developments, such as the preparation of guidelines and dedicated instrumental development to mitigate alteration that could be further developed in the course of international initiatives [141].

When analyzing cultural heritage artifacts by intense sources, radiation damage is an essential consideration and a concern of curators, conservators, archaeologists, paleontologists, analytical scientists and other professionals. In some cases, due to the large amount of energy deposited when performing these measurements, there is a risk of degradation of the materials under study. The application of high doses is often necessary, given that the sensitivity of most currently available detectors is limited and that trace information is often sought. Damage can sometimes be visible to the human eye (e.g., formation of color centers in glass, or browning of organic compounds). 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, can constitute a major analytical risk. We therefore proposed to redefine the terminology of damage in these materials by conserving the widely-used term "damage" to effects leading to changes noticeable through visible assessment, while we suggest using "radiation-induced side effects" to cover all alteration phenomena involving characterization.

We reviewed works describing alteration effects on different types of cultural heritage materials. From the discussion presented in this review, it is clear that intense radiation effects can occur in cultural heritage materials. These effects can be temporary, delayed or permanent, visible or non-visible, and can change the macroscopic, microscopic and molecular properties of these materials. As a result of the importance of cultural heritage materials, maintaining the integrity of the object by minimizing the effect of radiation, while obtaining maximum information, must be the most important task of the investigators. According to present practice, the criterion for assessing whether damage occurs or not, and to what extent, relies mostly on visual inspection. This criterion will be efficient in determining effects leading to significant changes in the material response in the optical region, but sometimes gives little or no insight into the presence of molecular or atomic level changes within the analyzed material. However, development of modern analytical techniques has provided us with the opportunity to move beyond visual inspection and look at atomic and molecular levels to determine the effect of intense radiation on cultural heritage materials. Advanced separation and MS or proteomics techniques, and highresolution hyperspectral imaging, allow assessment of damage down to molecular and atomic levels, thereby enabling a deeper level of understanding of fundamental damage processes and their implications for heterogeneous cultural heritage materials. Such a deeper level of understanding would enable us to improve how we address and mitigate radiation damage in cultural heritage materials.

In the specific field of cultural heritage, a concern is that the potential risk of alteration at atomic or molecular levels may be overinterpreted by curators and conservators, resulting in reduced collaboration. In addition, public perception of the damage to valuable, well-loved objects may be out of scale to the scientific debate, resulting in undue pressure to discourage further collaboration. These perceptions may prompt some scientists not to insist on the effects of radiation damage when working with curators and conservators. This can ease the development of a taboo where radiation damages are ignored rather than considered. We therefore suggest fostering joint initiatives and exchange of ideas between curators and scientists in order to develop a common approach. The discussion should also shift from policy regarding the irradiation of single objects to the definition of rules regarding categories or collections of objects and samples. New collaborative research programs with corresponding training actions can help to mitigate, to understand and to predict in a more precise way the effects of irradiation. As a more general consideration, we think that this process initiated in the scientific community involved in cultural heritage may be relevant to scientists working on many other classes of materials using intense radiation sources.

Authors' contributions

LB, MB and AS coordinated the preparation of the manuscript. All the authors contributed to the manuscript. All the authors read and approved the final manuscript. Specific questions can be addressed directly to individual authors as per their expertise: synchrotron analysis of ancient materials (LB: loic.bertrand@ synchrotron-soleil.fr, MBHB: phymbhb@nus.edu.sg, KJ: koen.janssens@ua.ac.be, SS: sebastian.schoeder@synchrotronsoleil.fr), laser analysis of ancient materials (DA: anglos@iesl .forth.gr), effect of radiation on proteinaceous materials (MM: moinim@gwu.edu), and IBA of ancient materials (MBHB, AS: a.simon@atomki.hu).

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References

- T. Calligaro, J.-C. Dran, J. Salomon, P. Walter, Review of accelerator gadgets for art and archaeology, Nucl. Instrum. Methods Phys. Res. B 226 (2004) 29–37.
- [2] N. Grassi, L. Giuntini, P.A. Mandò, M. Massi, Advantages of scanning-mode ion beam analysis for the study of Cultural Heritage, Nucl. Instrum. Methods Phys. Res. B 256 (2007) 712–718.
- [3] J. Salomon, J.-C. Dran, T. Guillou, B. Moignard, L. Pichon, P. Walter, et al., Present and future role of ion beam analysis in the study of cultural heritage materials: the example of the AGLAE facility, Nucl. Instrum. Methods Phys. Res. B 266 (2008) 2273–2278.
- [4] L. Pichon, L. Beck, P. Walter, B. Moignard, T. Guillou, A new mapping acquisition and processing system for simultaneous PIXE-RBS analysis with external beam, Nucl. Instrum. Methods Phys. Res. B 268 (2010) 2028–2033.
- [5] A. Zucchiatti, F. Agulló-Lopez, Potential consequences of ion beam analysis on objects from our cultural heritage: an appraisal, Nucl. Instrum. Methods Phys. Res. B 278 (2012) 106–114.
- [6] W.-K. Chu, J.W. Mayer, M.-A. Nicolet, Backscattering Spectrometry, Academic Press Inc., New-York, USA, 1978.
- [7] Y. Wang, M.A. Nastasi, Handbook of Modern Ion Beam Materials Analysis, Cambridge University Press, 2010.
- [8] L. Bertrand, M. Cotte, M. Stampanoni, M. Thoury, F. Marone, S. Schöder, Development and trends in synchrotron studies of ancient and historical materials, Phys. Rep. 519 (2012) 51–96.
- [9] M. Thoury, J.-P. Echard, M. Réfrégiers, B. Berrie, A. Nevin, F. Jamme, et al., Synchrotron UV-visible multispectral luminescence micro-imaging of historical samples, Anal. Chem. 83 (2011) 1737–1745.
- [10] M. Cotte, J. Susini, J. Dik, K. Janssens, Synchrotron-based X-ray absorption spectroscopy for art conservation: looking back and looking forward, Acc. Chem. Res. 43 (2010) 705–714.
- [11] P. Tafforeau, R. Boistel, E. Boller, A. Bravin, M. Brunet, Y. Chaimanee, et al., Applications of X-ray synchrotron microtomography for non-destructive 3D studies of paleontological specimens, Appl. Phys. A 83 (2006) 195– 202.
- [12] J. Dik, K. Janssens, G. van der Snickt, L. van der Loeff, K. Rickers, M. Cotte, Visualization of a lost painting by Vincent van Gogh using synchrotron radiation based x-ray fluorescence elemental mapping, Anal. Chem. 80 (2008) 6436–6442.
- [13] L. Bertrand, L. Robinet, M. Thoury, K. Janssens, S.X. Cohen, S. Schöder, Cultural heritage and archaeology materials studied by synchrotron spectroscopy and imaging, Appl. Phys. A 106 (2012) 377–396.
- [14] C. Fotakis, D. Anglos, V. Zafiropulos, S. Georgiou, V. Tornari, Lasers in the Preservation of Cultural Heritage. Principles and Applications, Taylor and Francis, New York, USA, 2006.
- [15] D. Anglos, M. Solomidou, I. Zergioti, V. Zafiropulos, T.G. Papazoglou, C. Fotakis, Laser-induced fluorescence in artwork diagnostics: an application in pigment analysis, Appl. Spectrosc. 50 (1996) 1331–1334.
- [16] G.D. Smith, R.J. Clark, Raman microscopy in art history and conservation science, Stud. Conserv. 46 (2001) 92–106.
- [17] P. Vandenabeele, Raman spectroscopy in art and archaeology, J. Raman Spectrosc. 35 (2004) 607–609.
- [18] P. Pouli, A. Selimis, S. Georgiou, C. Fotakis, Recent studies of laser science in paintings conservation and research, Acc. Chem. Res. 43 (2010) 771–781.
- [19] V. Tornari, Laser interference-based techniques and applications in structural inspection of works of art, Anal. Bioanal. Chem. 387 (2007) 761–780.
- [20] V. Tornari, E. Tsiranidou, E. Bernikola, Interference fringe-patterns association to defect-types in artwork conservation: an experiment and research validation review, Appl. Phys. A 106 (2012) 397–410.
- [21] M.A. Pollard, C. Heron, Archaeological Chemistry, Royal Society of Chemistry, London, UK, 2008.
- [22] C. Renfrew, P. Bahn, Archaeology: Theories, Methods and Practice, third ed., Thames & Hudson, London, UK, 2000.
- [23] J.-P. Demoule, F. Giligny, A. Lehöerff, A. Schnapp, Guide des Méthodes de l'archéologie, La Découverte, 2005.
- [24] K. Nassau, The Physics and Chemistry of Color: The Fifteen Causes of Color, second ed., Wiley-VCH, 2001.
- [25] J. Absil, H.-P. Garnir, D. Strivay, C. Oger, G. Weber, Study of color centers induced by PIXE irradiation, Nucl. Instrum. Methods Phys. Res. B 198 (2002) 90–97.
- [26] P.D. Townsend, P. Chandler, L. Zhang, Optical effects of ion implantation, in: Cambridge Studies in Modern Optics, vol. 13, Cambridge University Press, Cambridge, UK, 2006.

- [27] G.D. Richards, R.S. Jabbour, C.F. Horton, C.L. Ibarra, A.A. MacDowell, Color changes in modern and fossil teeth induced by synchrotron microtomography, Am. J. Phys. Anthropol. 149 (2012) 172–180.
- [28] O. Enguita, T. Calderón, M. Fernández-Jiménez, P. Beneitez, A. Millan, G. García, Damage induced by proton irradiation in carbonate based natural painting pigments, Nucl. Instrum. Methods Phys. Res. B 219–220 (2004) 53–56.
- [29] P. Milota, I. Reiche, A. Duval, O. Forstner, H. Guicharnaud, W. Kutschera, et al., PIXE measurements of Renaissance silverpoint drawings at VERA, Nucl. Instrum. Methods Phys. Res. B 266 (2008) 2279–2285.
- [30] G. Grime, Non-destructive ion beam analysis techniques for book and manuscript studies, Ch. 10, in: S. Neate, D. Howell, R. Ovenden, A. Pollard (Editors), The Technological Study of Books and Manuscripts as Artefacts, Research questions and analytical solutions, BAR S2209, British Archaeol. Rep., 2011, pp. 77–84.
- [31] B. Grieshaber, D. Osborne, A. Doubleday, F. Kaestle, A pilot study into the effects of X-ray and computed tomography exposure on the amplification of DNA from bone, J. Archaeol. Sci. 35 (2008) 681–687.
- [32] S.C. Zapico, D.H. Ubelaker, Applications of physiological bases of ageing to forensic sciences. Estimation of age-at-death, Ageing Res. Rev. 12 (2013) 605–617.
- [33] A. Nevin, D. Anglos, S. Cather, A. Burnstock, The influence of visible light and inorganic pigments on fluorescence excitation emission spectra of egg-, caseinand collagen-based painting media, Appl. Phys. A 92 (2008) 69–76.
- [34] H. Tan, H. Tian, J. Verbeeck, L. Monico, K. Janssens, G. Van Tendeloo, Nanoscale investigation of the degradation mechanism of a historical chrome yellow paint by quantitative electron energy loss spectroscopy mapping of chromium species, Angew. Chem. Int. Ed Engl. 52 (2013) 11360–11363.
- [35] L. Bertrand, M. Thoury, E. Anheim, Ancient materials specificities for their synchrotron examination and insights into their epistemological implications, J. Cult. Herit. 14 (2013) 277–289.
- [36] E.V. Sayre, R.W. Dodson, D.B. Thompson, Neutron activation study of Mediterranean potsherds, Am. J. Archaeol. 61 (1957) 35–41.
- [37] A.M. Pollard, C. Batt, B. Stern, S.M.M. Young, Analytical Chemistry in Archaeology, Manuals in Archaeology, Cambridge University Press, Cambridge, UK, 2007.
- [38] T. Calligaro, J.-C. Dran, J. Salomon, Ion beam microanalysis, Ch. 5, in: K. Janssens, R.E. van Grieken (Editors), Comprehensive Analytical Chemistry, vol. XLII, Elsevier, Amsterdam, 2004, pp. 227–276.
- [39] A. Roy, The laser microspectral analysis of paint, Natl. Gallery Tech. Bull. 3 (1979) 43–50.
- [40] L. Moenke-Blankenburg, Laser micro analysis, Prog. Anal. Spectrosc. 9 (1986) 335–427.
- [41] D. Anglos, S. Couris, C. Fotakis, Laser diagnostics of painted artworks: laserinduced breakdown spectroscopy in pigment identification, Appl. Spectrosc. 51 (1997) 1025–1030.
- [42] M. Delhaye, P. Dhamelincourt, Raman microprobe and microscope with laser excitation, J. Raman Spectrosc. 3 (1975) 33–43.
- [43] F. Cariati, S. Bruni, Raman spectroscopy, Ch. 10, in: E. Ciliberto, G. Spoto (Editors), Modern Analytical Methods in Art and Archaeology, Chemical Analysis, John Wiley & Sons, Ltd, New York, USA, 2000, pp. 255–278.
- [44] R.J.H. Clark, Raman microscopy: application to the identification of pigments on medieval manuscripts, Chem. Soc. Rev. 24 (1995) 187–196.
- [45] G.D. Smith, R.J.H. Clark, Raman microscopy in archaeological science, J. Archaeol. Sci. 31 (2004) 1137–1160.
- [46] B. Guineau, Analyse non destructive des pigments par microsonde raman laser: exemples de l'azurite et de la malachite, Stud. Conserv. 29 (1984) 35–41.
- [47] T. Miyoshi, M. Ikeya, S. Kinoshita, T. Kushida, Laser-induced fluorescence of oil colours and its application to the identification of pigments in oil paintings, Jpn. J. Appl. Phys. 21 (1982) 1032–1036.
- [48] D. Comelli, C. D'Andrea, G. Valentini, R. Cubeddu, C. Colombo, L. Toniolo, Fluorescence lifetime imaging and spectroscopy as tools for nondestructive analysis of works of art, Appl. Opt. 43 (2004) 2175–2183.
- [49] G. Filippidis, E.J. Gualda, K. Melessanaki, C. Fotakis, Nonlinear imaging microscopy techniques as diagnostic tools for art conservation studies, Opt. Lett. 33 (2008) 240–242.
- [50] G. Latour, J.-P. Echard, M. Didier, M.-C. Schanne-Klein, In situ 3D characterization of historical coatings and wood using multimodal nonlinear optical microscopy, Opt. Express 20 (2012) 24623–24635.
- [51] J. Lang, A. Middleton, Radiography of Cultural Material, Elsevier, Oxford, UK, 2005.
- [52] B.L. Henke, E. Gullikson, J. Davis, X-ray interactions: photoabsorption, scattering, transmission, and reflection at E = 50–30000 eV, Z = 1–92, At. Data Nucl. Data Tables 54 (1993) 181–342.
- [53] G. Harbottle, B.M. Gordon, K.W. Jones, Use of synchrotron radiation in archeometry, Nucl. Instrum. Methods Phys. Res. B 14 (1986) 116–122.
- [54] I. Brissaud, P. Chevallier, C. Dardenne, N. Deschamps, J.P. Frontier, K. Gruel, et al., Analysis of Gaulish coins by proton induced X-ray emission, synchrotron radiation X-ray fluorescence and neutron activation analysis, Nucl. Instrum. Methods Phys. Res. B 49 (1990) 305–308.
- [55] P.F. Schofield, G. Cressey, W. Wren Howard, C.M.B. Henderson, Origin of color in iron and manganese containing glasses investigated by synchrotron radiation, Glass Technol. 36 (1995) 89–94.
- [56] L. Bertrand, J. Doucet, P. Dumas, A. Simionovici, G. Tsoucaris, P. Walter, Microbeam synchrotron imaging of hairs from Ancient Egyptian mummies, J. Synchrotron Radiat. 10 (2003) 387–392.

- [57] L. Bertrand, M. Réfrégiers, B. Berrie, J.-P. Echard, M. Thoury, A multiscalar photoluminescence approach to discriminate among semiconducting historical zinc white pigments, Analyst 138 (2013) 4463–4669.
- [58] M. Alfeld, D.P. Siddons, K. Janssens, J. Dik, A.R. Woll, R. Kirkham, et al., Visualizing the 17th century underpainting in Portrait of an Old Man by Rembrandt van Rijn using synchrotron-based scanning macro-XRF, Appl. Phys. A 111 (2013) 157–164.
- [59] P. Gueriau, C. Mocuta, D.B. Dutheil, S.X. Cohen, D. Thiaudière, the OT1 consortium, et al., Trace elemental imaging of rare earth elements discriminates tissues at microscale in flat fossils, PLoS ONE 9 (2014) e86946.
 [60] E.F. Garman, R.L. Owen, Cryocooling and radiation damage in macromolecular
- crystallography, Acta Crystallogr. D Biol. Crystallogr. 62 (2005) 32–47.
- [61] P. Pouli, M. Oujja, M. Castillejo, Practical issues in laser cleaning of stone and painted artefacts: optimisation procedures and side effects, Appl. Phys. A 106 (2012) 447–464.
- [62] P. Pouli, C. Fotakis, B. Hermosin, C. Saiz-Jimenez, C. Domingo, M. Oujja, et al., The laser-induced discoloration of stonework; a comparative study on its origins and remedies, Spectrochim. Acta [A.] 71 (2008) 932–945.
- [63] M. Lassithiotaki, A. Athanassiou, D. Anglos, S. Georgiou, C. Fotakis, Photochemical effects in the UV laser ablation of polymers: implications for laser restoration of painted artworks, Appl. Phys. A 69 (1999) 363–367.
- [64] M. Castillejo, M. Martin, M. Oujja, D. Silva, R. Torres, A. Manousaki, et al., Analytical study of the chemical and physical changes induced by KrF laser cleaning of tempera paints, Anal. Chem. 74 (2002) 4662–4671.
- [65] J. Kolar, M. Stilic, M. Marincek, IR pulsed laser light interaction with soiled cellulose and paper, Appl. Phys. A 75 (2002) 673–676.
- [66] G. Demortier, Report on the Workshop on Damage induced by ion beams, LARN, Namur, Belgium, 18–19 Feb. 1997. COST Action G1, Application of ion beam analysis to art or archaeological objects, 1997.
- [67] D. Benzeggouta, I. Vickridge, Spirit Damage Handbook. Handbook on Best Practice for Minimising Beam Induced Damage during IBA, Handbook, Spirit Integrated Infrastructure Initiative, 2011.
- [68] P. Meyers, M.J. Cotter, L. van Zelst, E.V. Sayre, Art and autoradiography: insights into the genesis of paintings by Rembrandt, Van Dyck, and Vermeer, Ch. 3, in: M.W. Ainsworth (Editor), The Technical Procedures and the Effects of Radiation Exposure upon Paintings, The Metropolitan Museum of Art, New York, USA, 1982, pp. 105–110.
- [69] J. Monnier, S. Réguer, D. Vantelon, P. Dillmann, D. Neff, I. Guillot, X-rays absorption study on medieval corrosion layers for the understanding of very long-term indoor atmospheric iron corrosion, Appl. Phys. A 99 (2010) 399–406.
- [70] S. Réguer, P. Dillmann, F. Mirambet, J. Susini, P. Lagarde, Investigation of Cl corrosion products of iron archaeological artefacts using micro-focused synchrotron X-ray absorption spectroscopy, Appl. Phys. A 83 (2006) 189– 193.
- [71] A.F. Gualtieri, P. Venturelli, In situ study of the goethite-hematite phase transformation by real time synchrotron powder diffraction, Am. Mineral. 84 (1999) 895–904.
- [72] R. Bruder, D.L. Hermite, A. Semerok, L. Salmon, V. Detalle, Near-crater discoloration of white lead in wall paintings during laser induced breakdown spectroscopy analysis, Spectrochim. Acta Part B At. Spectrosc. 62 (2007) 1590–1596.
- [73] C. Gervais, M.-A. Languille, S. Reguer, M. Gillet, E.P. Vicenzi, S. Chagnot, et al., "Live" Prussian blue fading by time-resolved X-ray absorption spectroscopy, Appl. Phys. A 111 (2013) 15–22.
- [74] C. Gervais, M.-A. Languille, S. Reguer, M. Gillet, S. Pelletier, C. Garnier, et al., Why does Prussian blue fade? Understanding the role(s) of the substrate, J. Anal. At. Spectrom. 28 (10) (2013) 1600–1609.
- [75] L. Monico, K. Janssens, C. Miliani, B.G. Brunetti, M. Vagnini, F. Vanmeert, et al., Degradation process of lead chromate in paintings by Vincent van Gogh studied by means of spectromicroscopic methods. 3. Synthesis, characterization, and detection of different crystal forms of the chrome yellow pigment, Anal. Chem. 85 (2013) 851–859.
- [76] G. Bounos, A. Athanassiou, D. Anglos, S. Georgiou, Dynamics of dopant product formation in the nanosecond irradiation of doped PMMA at 248 and 193 nm: temporal evolution of temperature and viscosity, Chem. Phys. Lett. 418 (2006) 317–322.
- [77] P. Whitmore, P. Xun, C. Bailie, Predicting the fading of objects: identification of fugitive colorants through direct nondestructive lightfastness measurements, J. Am. Inst. Conserv. 38 (1999) 395–409.
- [78] A. Simon, R. Huszank, M. Novák, Z. Pintye, Investigation of hydrogen depletion of organic materials upon ion beam irradiation by simultaneous micro-RBS and micro-ERDA techniques, Nucl. Instrum. Methods Phys. Res. B 268 (2010) 2197–2201.
- [79] B. Kanngiesser, O. Hahn, M. Wilke, B. Nekat, W. Malzer, A. Erko, Investigation of oxidation and migration processes of inorganic compounds in ink-corroded manuscripts, Spectrochim. Acta Part B At. Spectrosc. 59 (2004) 1511–1516.
- [80] M. Wilke, O. Hahn, A.B. Woodland, K. Rickers, The oxidation state of iron determined by Fe K-edge XANES-application to iron gall ink in historical manuscripts, J. Anal. At. Spectrom. 24 (2009) 1364–1372.
- [81] V. Mazel, P. Richardin, D. Debois, D. Touboul, M. Cotte, A. Brunelle, et al., Identification of ritual blood in African artifacts using TOF-SIMS and synchrotron radiation microspectroscopies, Anal. Chem. 79 (2007) 9253–9260.
- [82] M. Moini, K. Klauenberg, M. Ballard, Dating silk by capillary electrophoresis mass spectrometry, Anal. Chem. 83 (2011) 7577–7581.

- [83] M. Sandström, F. Jalilehvand, I. Persson, U. Gelius, P. Frank, I. Hall-Roth, Deterioration of the seventeenth-century warship Vasa by internal formation of sulphuric acid, Nature 415 (2002) 893–897.
- [84] M. Moini, C. Rollman, R. Fleskes, Molecular level effects of natural aging, as well as chemical and radiation exposures on museums' proteinaceous specimens, in: Proceedings of American Society for Mass Spectrometry Meeting 2013, 2014.
- [85] M. Moini, C.M. Rollman, L. Bertrand, Assessing the impact of synchrotron x-ray irradiation on proteinaceous specimens at macro and molecular levels, Anal. Chem. 86 (2014) 9417–9422.
- [86] M. Mantler, J. Klikovits, Analysis of art objects and other delicate samples: Is XRF really nondestructive?, Powder Diffr. 19 (2004) 16–20.
- [87] K. Patten, L. Gonzalez, C. Kennedy, D. Mills, G. Davis, T. Wess, Is there evidence for change to collagen within parchment samples after exposure to an X-ray dose during high contrast X-ray microtomography? A multi technique investigation, Herit. Sci. 1 (2013) 22.
- [88] U. Paredes, R. Prys-Jones, M. Adams, J. Groombridge, S. Kundu, P. Agapow, et al., Micro-CT X-rays do not fragment DNA in preserved bird skins, J. Zoolog. Syst. Evol. Res. 50 (2012) 247–250.
- [89] E.L. Alpen, Radiation Biophysics, Academic Press, 1997.
- [90] M. Folkard, K.M. Prise, G. Grime, K. Kirkby, B. Vojnovic, The use of microbeams to investigate radiation damage in living cells, Appl. Radiat. Isot. 67 (2009) 436–439.
- [91] H.D. Barth, M.E. Launey, A.A. MacDowell, J.W. Ager III, R.O. Ritchie, On the effect of X-ray irradiation on the deformation and fracture behavior of human cortical bone, Bone 46 (2010) 1475–1485.
- [92] J.M. Holton, A beginner's guide to radiation damage, J. Synchrotron Radiat. 16 (2009) 133–142.
- [93] M. Warkentin, J.B. Hopkins, R. Badeau, A.M. Mulichak, L.J. Keefe, R.E. Thorne, Global radiation damage: temperature dependence, time dependence and how to outrun it, J. Synchrotron Radiat. 20 (2013) 7–13.
- [94] R. Sanishvili, D.W. Yoder, S.B. Pothineni, G. Rosenbaum, S. Xu, S. Vogt, et al., Radiation damage in protein crystals is reduced with a micron-sized x-ray beam, Proc. Natl. Acad. Sci. U.S.A. 108 (2011) 6127–6132.
- [95] R.B.G. Ravelli, S.M. McSweeney, The 'fingerprint' that X-rays can leave on structures, Structure 8 (2000) 315–328.
- [96] D. Liebschner, M. Dauter, G. Rosenbaum, Z. Dauter, How good can our beamlines be?, Acta Crystallogr. D Biol. Crystallogr. 68 (2012) 1430–1436.
- [97] B. Akabayov, C.J. Doonan, I.J. Pickering, G.N. George, I. Sagi, Using softer X-ray absorption spectroscopy to probe biological systems, J. Synchrotron Radiat. 12 (2005) 392–401.
- [98] S. George, J. Fu, Y. Guo, O. Drury, S. Friedrich, T. Rauchfuss, et al., X-ray photochemistry in iron complexes from Fe(0) to Fe(IV) – can a bug become a feature?, Inorganica Chim. Acta 361 (2008) 1157–1165.
- [99] J. Kirz, C. Jacobsen, M. Howells, Soft X-ray microscopes and their biological applications, Q. Rev. Biophys. 28 (1995) 33–130.
- [100] A. Manceau, M.A. Marcus, N. Tamura, O. Proux, N. Geoffroy, B. Lanson, Natural speciation of Zn at the micrometer scale in a clayey soil using X-ray fluorescence, absorption, and diffraction, Geochim. Cosmochim. Acta 68 (2004) 2467–2483.
- [101] E. Teo, B. Xiong, Y. Ow, M.B.H. Breese, A. Bettiol, Effects of oxide formation around core circumference of silicon-on-oxidized-porous-silicon strip waveguides, Opt. Lett. 34 (2009) 3142–3144.
- [102] T.R. Oldham, F. McLean, Total ionizing dose effects in MOS oxides and devices, IEEE Trans. Nucl. Sci. 50 (2003) 483–499.
- [103] M.I. Ojovan, W.E. Lee, An Introduction to Nuclear Waste Immobilisation, vol. 7, Elsevier, Amsterdam, 2005.
- [104] M.B.H. Breese, G. Grime, M. Dellith, The effect of ion induced damage on IBIC images, Nucl. Instrum. Methods Phys. Res. B 77 (1993) 332–338.
- [105] F. Uhlén, D. Nilsson, A. Holmberg, H.M. Hertz, C.G. Schroer, F. Seiboth, et al., Damage investigation on tungsten and diamond diffractive optics at a hard X-ray free-electron laser, Opt. Express 21 (2013) 8051–8061.
- [106] K. Nygard, S. Gorelick, J. Vila-Comamala, E. Farm, A. Bergamaschi, A. Cervellino, et al., Beam-induced damage on diffractive hard X-ray optics, J. Synchrotron Radiat. 17 (2010) 786–790.
- [107] M.J. Madou, Fundamentals of Microfabrication and Nanotechnology: Manufacturing Techniques for Microfabrication and Nanotechnology, vol. 2, CRC Press, Boca Raton, Florida, USA, 2011.
- [108] E. Rimini, Ion Implantation: Basics to Device Fabrication, vol. 293, Springer, 1995.
- [109] E. Rightor, A. Hitchcock, H. Ade, R. Leapman, S. Urquhart, A. Smith, et al., Spectromicroscopy of poly(ethylene terephthalate): comparison of spectra and radiation damage rates in X-ray absorption and electron energy loss, J. Phys. Chem. B 101 (1997) 1950–1960.
- [110] R.J. Davies, M. Burghammer, C. Riekel, A combined microRaman and microdiffraction set-up at the European Synchrotron Radiation Facility ID13 beamline, J. Synchrotron Radiat. 16 (2009) 22–29.
- [111] T. Beetz, C. Jacobsen, Soft X-ray radiation-damage studies in PMMA using a cryo-STXM, J. Synchrotron Radiat. 10 (2003) 280–283.
- [112] J. Wang, C. Morin, L. Li, A.P. Hitchcock, A. Scholl, A. Doran, Radiation damage in soft X-ray microscopy, J. Electron Spectros. Relat. Phenomena 170 (2009) 25–36.
- [113] R. Huszank, D. Szikra, A. Simon, S.Z. Szilasi, I.P. Nagy, ⁴He⁺ ion beam irradiation induced modification of poly(dimethylsiloxane). Characterization by infrared spectroscopy and ion beam analytical techniques, Langmuir 27 (2011) 3842–3848.

- [114] M. Wisniewski, A. Sionkowska, H. Kaczmarek, S. Lazare, V. Tokarev, C. Belin, Spectroscopic study of a KrF excimer laser treated surface of the thin collagen films, J. Photochem. Photobiol. A Chem. 188 (2007) 192–199.
- [115] M. Wilmanns, Future structural biology applications with a free-electron laser-more than wild dreams?, J. Synchrotron Radiat. 7 (2000) 41–46.
- [116] O. Carugo, K.D. Carugo, When X-rays modify the protein structure: radiation damage at work, Trends Biochem. Sci. 30 (2005) 213–219.
- [117] M. Weik, R.B. Ravelli, G. Kryger, S. McSweeney, M.L. Raves, M. Harel, et al., Specific chemical and structural damage to proteins produced by synchrotron radiation, Proc. Natl. Acad. Sci. U.S.A. 97 (2000) 623–628.
- [118] J.P. Maity, S. Chakraborty, S. Kar, S. Panja, J.-S. Jean, A.C. Samal, et al., Effects of gamma irradiation on edible seed protein, amino acids and genomic DNA during sterilization, Food Chem. 114 (2009) 1237–1244.
- [119] F. Wien, A. Miles, J. Lees, S.V. Hoffmann, B. Wallace, VUV irradiation effects on proteins in high-flux synchrotron radiation circular dichroism spectroscopy, J. Synchrotron Radiat. 12 (2005) 517–523.
- [120] A. Yamashita, T. Dotani, M. Bautz, G. Crew, H. Ezuka, K. Gendreau, et al., Radiation damage to charge coupled devices in the space environment, IEEE Trans. Nucl. Sci. 44 (1997) 847–853.
- [121] F.A. Cucinotta, W. Schimmerling, J.W. Wilson, L.E. Peterson, G.D. Badhwar, P.B. Saganti, et al., Space radiation cancer risks and uncertainties for Mars missions, Radiat. Res. 156 (2001) 682–688.
- [122] G. Kminek, J.L. Bada, The effect of ionizing radiation on the preservation of amino acids on Mars, Earth Planet. Sci. Lett. 245 (2006) 1–5.
- [123] C. Jacobsen, J. Kirz, X-ray microscopy with synchrotron radiation, Nat. Struct. Biol. 5 (1998) 650–653.
- [124] A. Michelin, E. Drouet, E. Foy, J.J. Dynes, D. Neff, P. Dillmann, Investigation at the nanometre scale on the corrosion mechanisms of archaeological ferrous artefacts by STXM, J. Anal. At. Spectrom. 28 (2013) 59–66.
- [125] A.P. Hitchcock, J.J. Dynes, G. Johansson, J. Wang, G. Botton, Comparison of NEXAFS microscopy and TEM-EELS for studies of soft matter, Micron 39 (2008) 311–319.
- [126] M. Howells, T. Beetz, H. Chapman, C. Cui, J. Holton, C. Jacobsen, et al., An assessment of the resolution limitation due to radiation-damage in X-ray diffraction microscopy, J. Electron Spectros. Relat. Phenomena 170 (2009) 4–12.
- [127] B.C. Garrett, D.A. Dixon, D.M. Camaioni, D.M. Chipman, M.A. Johnson, C.D. Jonah, et al., Role of water in electron-initiated processes and radical chemistry: issues and scientific advances, Chem. Rev. 105 (2005) 355–389.
- [128] H. Bichsel, D.E. Groom, S.R. Klein, Passage of particles through matter, Phys. Lett. B 667 (2008) 267–280.

- [129] D. Anglos, S. Georgiou, C. Fotakis, Lasers in the analysis of cultural heritage materials, J. Nano Res. 8 (2009) 47–60.
- [130] A. Nevin, G. Spoto, D. Anglos, Laser spectroscopies for elemental and molecular analysis in art and archaeology, Appl. Phys. A 106 (2) (2012) 339–361.
- [131] E. Esposito, L. Scalise, V. Tornari, Measurement of stress waves in polymers generated by UV laser ablation, Opt. Lasers Eng. 38 (2002) 207–215.
- [132] U. Bergmann, P.L. Manning, R.A. Wogelius, Chemical mapping of paleontological and archeological artifacts with synchrotron X-rays, Annu. Rev. Anal. Chem. (Palo Alto Calif) 5 (2012) 361–389.
- [133] K. Medjoubi, N. Leclercq, F. Langlois, A. Buteau, S. Lé, S. Poirier, et al., Development of fast, simultaneous and multi-technique scanning hard X-ray microscopy at Synchrotron Soleil, J. Synchrotron Radiat. 20 (2013) 293–299.
- [134] K. Proost, K. Janssens, B. Wagner, E. Bulska, M. Schreiner, Determination of localized Fe²⁺/Fe³⁺ ratios in inks of historic documents by means of μ-XANES, Nucl. Instrum. Methods Phys. Res. B 213 (2004) 723–728.
- [135] A. Crabbé, M.-A. Languille, I. Vandendael, J. Hammons, M. Silly, G. Dewanckel, et al., Colorando auro: contribution to the understanding of a medieval recipe to color gilded silver plates, Appl. Phys. A 111 (2013) 39–46.
- [136] S. Cagno, G. Nuyts, S. Bugani, K. De Vis, O. Schalm, J. Caen, et al., Evaluation of manganese-bodies removal in historical stained glass windows via SR-XANES/XRF and SR-µ-CT, J. Anal. At. Spectrom. 26 (2011) 2442–2451.
- [137] C. Ryan, R. Kirkham, R. Hough, G. Moorhead, D. Siddons, M. de Jonge, et al., Elemental X-ray imaging using the Maia detector array: the benefits and challenges of large solid-angle, Nucl. Instrum. Methods Phys. Res. A 619 (2010) 37–43.
- [138] M.B.H. Breese, G. Grime, F. Watt, The nuclear microprobe, Annu. Rev. Nucl. Part. Sci. 42 (1992) 1–38.
- [139] C. Zhou, M. Li, R. Garcia, A. Crawford, K. Beck, D. Hinks, et al., Time-of-flightsecondary ion mass spectrometry method development for high-sensitivity analysis of acid dyes in nylon fibers, Anal. Chem. 84 (2012) 10085–10090.
- [140] M. Chukalina, A. Simionovici, S. Zaitsev, C.J. Vanegas, Quantitative comparison of X-ray fluorescence microtomography setups: standard and confocal collimator apparatus, Spectrochim. Acta Part B At. Spectrosc. 62 (2007) 544–548.
- [141] A. Adriaens, European actions to promote and coordinate the use of analytical techniques for cultural heritage studies, Trends Analyt. Chem. 23 (2004) 583–586.