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Introduction to Synchrotron Radiation: Application to the Study of Cultural Heritage Materials and Biominerals

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1.1. Introduction

Cultural Heritage materials are often complex and heterogeneous with a hierarchical architecture spanning from the nanometer range to the macroscopic. An ancient ceramic is usually made of a clay body, on which a surface decoration is apposed (clay patterning, slip, glaze, etc.). The chemical and structural composition of the raw materials and the firing technique (temperature and atmosphere control) affect the end quality and intrinsic properties of the product for its everyday use. An ancient iron axe preserves traces of the manufacturing process in its inner structure, hinting at the know-how of the craftsman who manufactured it. The passing of time, storage conditions and conservation intervention are assessed by the presence of corrosion products and/or passivation layers at the surface of the axe. Cultural Heritage does not only refer to manufactured objects, but also encompasses the tools and techniques developed by ancient societies. In such a context, Roman concrete has shown exceptional resilience over time, as evidenced by Roman monuments still standing today after two millennia.

Synchrotron Radiation, Cultural Heritage, Biomineralization,
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Finally, preservation and conservation of our Cultural Heritage is of societal concern, a legacy from the past to be transmitted to future generations.

Cultural Heritage is at the junction of several disciplines, such as history, art, archaeology, materials science, chemistry, physics, geology and biology. The reasons for studying Cultural Heritage materials are diverse: knowledge of ancient societies, evolution of practices, development of trading exchanges, material properties, artifact dating, artwork preservation and restoration, etc. Today, the study of Cultural Heritage materials often requires scientific collaborations across multiple disciplines, necessitating combined approaches and promoting interactions between different scientific communities. The rarity, fragility and complexity of Cultural Heritage materials makes them challenging to study, justifying the use of the most advanced scientific tools such as synchrotron radiation facilities to decipher the secrets hidden in their structure.

Synchrotron radiation is the electromagnetic radiation emitted when charge particles travelling at relativistic velocities are radially accelerated. One of the most spectacular manifestations of synchrotron radiation is the Crab Nebula (and associated pulsar, a 30.2 Hz spinning neutron star), remnant of a supernova observed in 1054 by Chinese and Japanese astronomers (Figure 1.1a) (Burbidge 1957; Caroff and Scargle 1969; Bychkov 1973). The strong magnetic field produced by the pulsar bends the electron path, thus generating synchrotron radiation.

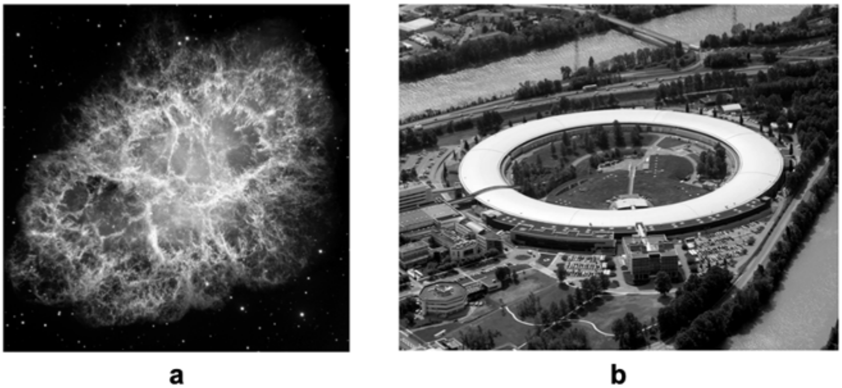

Figure 1.1. *a) Crab nebula mosaic image, taken by NASA Hubble Space Telescope (credit: NASA, ESA). b) View of the European Synchrotron Radiation Facility (ESRF), Grenoble, France (credit: ESRF/D. Morel). For a color version of this figure, see www.iste.co.uk/dejoie/synchrotron.zip*

Part of the theory around synchrotron radiation was formulated at the end of the 19th century (Liénard 1898). The first particle accelerators emerged in the first half of the 20th century, and synchrotron radiation was observed for the first time at General Electric in 1947 (Goward and Barnes 1946; Elder et al. 1947). In the beginning, such radiation, causing the particles to lose energy, was mainly seen as a nuisance in high-energy electron accelerators (Blewett 1998). Nevertheless, the possibility to produce X-rays of unprecedented brilliance was soon recognized. Synchrotron beams were first used in a parasitic way by scientists at particle accelerators. Today, more than 50 fully dedicated synchrotron sources exist, distributed all over the world (Figure 1.1b)[1].

Pioneering work using synchrotron radiation for the study of Cultural Heritage materials was performed in the 1990s at both the Synchrotron Radiation Source (SRS) at the Daresbury Laboratory in the UK (Pantos 2005) and at the European Synchrotron Radiation Facility (ESRF) in France (Walter et al. 1999). The use of synchrotron radiation for the study of Cultural Heritage materials is today more common. Over the last 20 years, the potential of such an approach, the main relevant synchrotron methods and their applications to Cultural Heritage material studies have been extensively reviewed (for example, Bertrand et al. 2012; Dejoie et al. 2018b; Cotte et al. 2019; Janssens and Cotte 2020). The same synchrotron tools used in Cultural Heritage materials are also relevant to other fields such as paleontology and biomineralization. Like in Cultural Heritage, seashells and other biominerals have a complex and multiscale hierarchical structure, the properties of which we have only started to understand. Millions of years of evolution have led nature to create materials that are unique in their properties and a new branch of science, biomimetics, which seeks to understand how nature does it and how we can create new materials with that knowledge.

The objective of this book is to show some recent applications of synchrotron radiation in the field of Heritage Science through a series of contributions about ancient ceramics, the corrosion of iron-based materials, the concrete used in Roman monuments and in the related field of biomineralization. In this introductory chapter, a few elements concerning synchrotron radiation will be briefly described, before introducing the contents of the book in more detail.

1.2. What is synchrotron radiation?

Synchrotron radiation is emitted when charged particles travelling at relativistic speed are accelerated in a curved trajectory. In a synchrotron facility, electrons are

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[1] See: https://lightsources.org/lightsources-of-the-world/.

circulated in a storage ring near the speed of light. They are guided by magnetic fields coming from bending magnets that cause deflection of their trajectory in the horizontal plane, generating synchrotron radiation tangentially to the electron orbit. The storage ring has a polygonal shape, made of a series of cells, alternating bending magnets and straight sections, with insertion devices (wigglers or undulators) sources occupying the straight sections (Figure 1.2a). Bending magnets generate a continuous polychromatic X-ray spectrum with maximum intensity at a bending magnet critical energy. Insertion devices are made of arrays of magnets that provide a sinusoidal magnetic field, thus causing the trajectory of the electrons to oscillate, and, in so doing, to emit synchrotron radiation at each trajectory bend. In an insertion device, each emission of synchrotron radiation either adds up to produce a photon energy spectrum similar to a bending magnet but brighter (wiggler) or interfere constructively at certain energies, resulting in a series of radiation peaks (called harmonics) an order of magnitude brighter than a bending magnet or wiggler (undulators). On each turn in the storage ring, radio frequency (RF) cavities, which contain electromagnetic fields oscillating at radio frequencies, restore the energy lost by the electrons as they circulate and emit synchrotron radiation (Figure 1.2a). Beamlines where synchrotron radiation is used (mainly X-ray photons, and also IR and gamma rays) are constructed tangentially from both bending magnets and straight sections. Additional information on synchrotron radiation can be found in Margaritondo (1988), Als-Nielsen and McMorrow (2001), Kim (2001), Fitch (2019) or Hwu and Margaritondo (2021).

The principle attributes of synchrotron radiation can be defined as follows:

– high brightness, so a highly collimated and intense beam emitted from a small source size, delivering high flux of photons to the sample. This brightness parameter will be discussed further in the next paragraphs;

– a tunable range of wavelengths, extending from infrared, to soft and hard X-ray regimes, depending on the synchrotron facility. A specific wavelength can be chosen, or variable energy used, for example, for spectroscopy;

– an X-ray beam with a certain degree of coherence that can be exploited for specific experiments, for example, ptychography;

– a polarized source, as the synchrotron radiation is normally linearly polarized in the plane of the synchrotron orbit;

– a pulsed source, as the electrons do not circulate individually in the storage ring but are confined in bunches. The distribution of the bunches allows the time structure to be exploited for specific experiments.

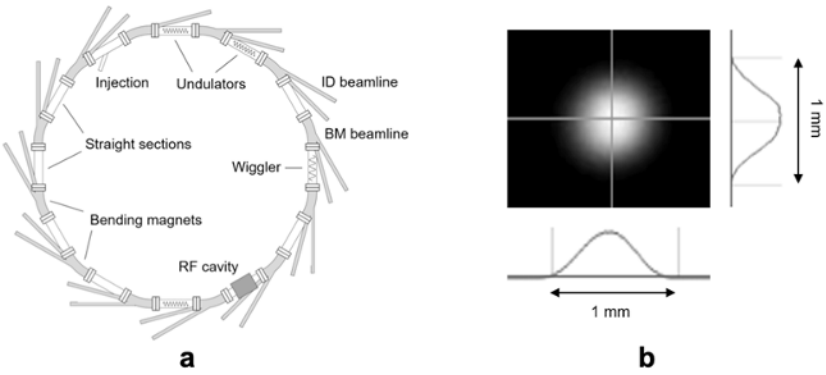

Figure 1.2. *a) Schematic representation of a synchrotron storage ring. Adapted from Fitch 2019. b) X-ray beam profile obtained at the ID22 beamline (ESRF) on September 2020. As a result of the EBS (Extremely Brilliant Source, see below) upgrade, the beam is quasi-symmetric. For a color version of this figure, see www.iste.co.uk/dejoie/synchrotron.zip*

Two parameters are often highlighted when discussing storage rings and beamline performance: the energy of the electrons in the storage ring and the spectral brightness (or brilliance). These two parameters will be discussed further in the next few paragraphs.

The energy E_e of the electrons circulating at a speed v is given by:

$$E_e = \frac{m_e c^2}{\sqrt{1 - v^2/c^2}} = \gamma m_e c^2$$

where m_e is the mass of the electron at rest ($m_e = 9.10938356 \times 10^{-31}$kg), and γ is the factor by which the mass of an electron increases because of its relativistic speed. After conversion of m_e in eV, the electron rest mass becomes 5.10998946×10^5 eV, and then the γ factor can be expressed as a function of the energy (in GeV), with

$$\gamma \approx 1957 E_e \text{ [GeV]}$$

Thus, for a 1.9-GeV (e.g. the Advanced Light Source (ALS), Berkeley, USA, optimized for the use of soft to medium energy X-rays) and a 6-GeV machine (e.g. the ESRF, Grenoble, France, optimized to access harder energy X-rays), γ takes a value of 3,718 and 11,742 respectively. The mass of an electron with an energy of 6 GeV is then roughly 10,000 times heavier than at rest. Expressed in atomic mass units, the mass of a 1.9-GeV electron and a 6-GeV electron is then 2.04 (comparable to the atomic mass of deuterium!) and 6.44 (almost a lithium atom!) respectively. Knowing the circumference and beam current of the synchrotron facility, the electron lap time, the number of laps per second or the expected number of electrons in the storage ring can also be calculated.

The second parameter, the brightness of a beamline, is defined as the number of X-ray photons per second, per 0.1% bandpass, per $mrad^2$, per mm^2, where 0.1% bandpass corresponds to a $\delta\lambda/\lambda$ of 0.001, $mrad^2$ is the solid-angle emission of the X-rays from the source and mm^2 is the cross-sectional area of the source. As a result, a high-brightness source produces (at a given energy) a lot of photons per second, into a narrow solid angle, with a small source size. The source size plays an important role and is strongly influenced by the electron beam properties, in particular its emittance. The lower the emittance, the smaller the source size, and thus the higher the resulting brightness. Lowering the horizontal emittance of the electron beam is the main challenge today, and a number of synchrotron facilities are currently undergoing or planning an upgrade to tackle this (e.g. Raimondi 2016; Sajaev 2019). In order to achieve this, the ESRF, the first among the third-generation facilities to achieve such an upgrade, has implemented a new ring lattice, the Hybrid Multi-bend Achromat (HMBA), based on an increase and a new arrangement of magnets within a cell. As a result, the horizontal divergence of the beam was reduced, and a more symmetric X-ray beam, of increased brightness, was obtained (Figure 1.2b). The new source, called EBS (Extremely Brilliant Source) became available to users in August 2020.

The X-ray source and the optical elements used to condition the X-ray beam differ from beamline to beamline and are chosen and tuned to best fit specific types of techniques and experiments (e.g. diffraction, spectroscopy, imaging, etc.). Bending magnet and wiggler sources provide a broad spectral range of X-ray photons and are more suited for polychromatic applications and techniques, where energy tunability is desirable (spectroscopy). An undulator source provides a sinusoidal magnetic field, so by choosing the period of the magnetic array and by varying the strength of the field, both wavelength distribution and X-ray beam divergence can be controlled. As well as its bending magnet or insertion device source, a beamline will incorporate a number of optical elements such as beam-size defining slits, a monochromator to select the wavelength, and focusing elements such as Kirkpatrick–Baez (KB) mirrors and compound refractive lenses (CRL). To illustrate this, the layout of two X-ray diffraction beamlines will be described in the next two paragraphs. The first beamline is dedicated to microdiffraction, thus providing high-spatial resolution for structural studies, while the second one is dedicated to high-angular resolution powder diffraction, for which the use of a larger beam of low divergence is favored.

Beamline 12.3.2 (ALS, Berkeley) is built on a superconducting magnet (or superbend) source, thus providing a continuous range of energy in the 5–24 keV range (Figure 1.3a). A grazing incidence toroidal mirror relays the source to the entrance of the experimental hutch. Two operation modes for single-crystal or powder diffraction measurements are provided, using either the full polychromatic (white) beam delivered by the superconducting magnet source or a monochromatic beam. A four-bounce monochromator allows for fast-switching between the two modes, while accurately maintaining the beam position on the sample. The X-ray beam is focused down to 0.5µm×0.5µm in polychromatic mode and 5µm×2µm in monochromatic mode using a pair of KB mirrors. Laue (white beam) microdiffraction has proven to be a successful approach to map at the micron scale crystal orientation and crystal distortion in polycrystalline and composite materials, including Cultural Heritage materials (Tamura et al. 2003; Kunz et al. 2009; Chen et al. 2016).

The ID22 beamline of the ESRF is built on an in-vacuum undulator source with a 26 mm magnetic period. The corresponding spectrum is shown in Figure 1.3b. The polychromatic beam delivered by the undulator source arrives untouched onto a cryogenically cooled channel-cut Si 111 monochromator, and, after passing a series of slits, a 1 mm × 1 mm highly monochromatic beam ($\Delta\lambda/\lambda \approx 10^{-4}$), of low divergence, is delivered to the sample. Aluminum-CRL can be inserted in the monochromatic beam as desired, for a resulting focusing down to 50 µm × 50 µm. The high-angular resolution of the powder pattern is ensured by the presence of analyzer crystals (e.g. perfect Si 111 crystals) intercepting the diffracted beam (Hodeau et al. 1998). As a result, the instrumental contribution to the full width at half maximum of a diffraction peak, measured on the NIST standard 640c Si 111 peak, is very small (< 0.0025° (2θ) at 31 keV); and this is exploited for a wide range of powder diffraction experiments (Fitch 2004; Dejoie et al. 2018a; Fitch et al. 2023).

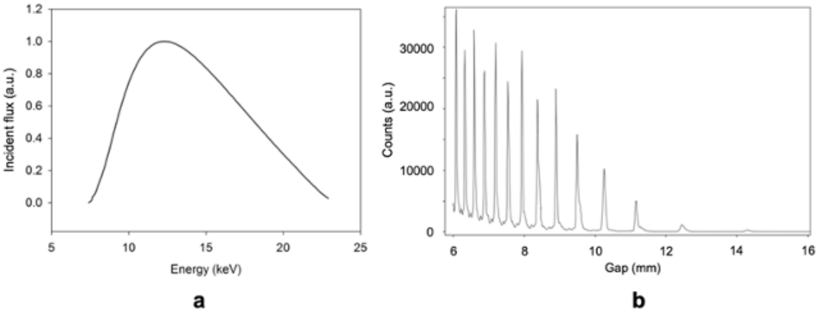

Figure 1.3. *a) Incident flux delivered by the Superbend source of the 12.3.2 beamline at ALS (extracted using the reverse method, Dejoie et al. 2011). b) Spectrum delivered by the U26 undulator of the ID22 beamline, ESRF (70 keV incident energy). For a color version of this figure, see www.iste.co.uk/dejoie/synchrotron.zip*

Synchrotron radiation facilities are user facilities, usually publicly funded. To gain access to a particular beamline and instrument, scientists from external academic or industrial laboratories submit scientific proposals. Proposals are peer-reviewed and accepted on the basis of their scientific merit. Users do not need to be experts in synchrotron radiation methods, as support is provided by the facility and the scientific and technical staff of the beamlines. Access to carry out proprietary research can also be arranged. Users can also form consortia around similar scientific interest and techniques and apply for beam time as is. This procedure is currently under implementation at the ESRF for Materials Science users (Streamline project) and will also benefit to the Cultural Heritage community through a dedicated BAG (Block Allocation Group) (Cotte et al. 2022).

1.3. Synchrotron radiation and Cultural Heritage

Owing to their non-standard shapes, their unique nature, their heterogeneity and sometimes multiscale and composite architecture, Cultural Heritage materials present some analytical challenges that synchrotron-based techniques may help to overcome. The intense beams provided by synchrotron facilities allow the study of samples via a series of X-ray based techniques, such as X-ray diffraction and scattering, X-ray absorption and emission spectroscopy, tomography and other imaging methods. The reasons to study Cultural Heritage materials can be diverse, but, most of the time, four main types of information are exploited:

– the chemical composition of the sample, using X-ray fluorescence (XRF);

– the oxidation state of the relevant chemical elements, using X-ray absorption spectroscopy (XAS);

– the structural composition of the sample using X-ray powder diffraction scattering (XRD) techniques, to retrieve information about the crystalline phases, and, in some cases, about the non-crystalline content;

– the general organization of the sample using two-dimensional and/or three-dimensional chemical (XRF, XAS) and structural (XRD) mapping. Most of the time, the spatial resolution that can be achieved is intrinsically linked to the size of the incident X-ray beam, so micro- to nano-size beams are favored.

Most of the examples described in this book will exploit one, or several of these four types of information, also combined with results obtained from lab-based techniques. In some cases, average information about the material is favored and macroprobes are used; while in others, information at a more local scale is necessary, thus requiring the use of micro- or nano-probes. It is often necessary to combine several approaches and results obtained from independent and complementary probes when materials related to Cultural Heritage are studied.

This book dedicated to Cultural Heritage and synchrotron radiation is divided into three parts. The first part is composed of a single contribution, covering the development of the use of synchrotron radiation for the study of Cultural Heritage materials, with the description of a few pertinent examples in the field of ancient ceramics, mural and oil paintings, rock art, cosmetics, manuscripts and paleontology.

The second, composed of two contributions, is oriented toward synchrotron method developments and the applications of synchrotron mapping techniques to Cultural Heritage materials and biomineralization. One unique feature provided by synchrotron facilities is the ability to generate high-brilliance micro- to nano-beams. These beams enable rapid chemical and structural mapping of relatively large regions within just a few minutes. This capability sets synchrotron facilities apart, offering researchers a powerful tool to explore and analyze materials with exceptional precision and efficiency. We choose to focus on two main techniques exploiting absorption and diffraction respectively, both of which show increasing interest in all areas of materials science. First, the full-field X-ray absorption spectroscopy imaging technique will be described, and a few applications in relation to Cultural Heritage will be presented, in the first contribution. The second technique we choose to highlight is X-ray diffraction – computed tomography (XRD-CT). The basic principle will be explained, before showing its potential for Cultural Heritage studies, in the second contribution.

The third part of the book is composed of four contributions, oriented toward the study of four different types of material for which synchrotron-based techniques have had significant impact. The first type of material is ceramics. Ceramics are among the first examples in history of a large-scale development of crafted objects, for everyday use, decoration or trading. The manufacturing process involves a series of steps, sometimes approaching the industrial scale, as in the case of *Terra Sigillata* ceramics (Sciau et al. 2006) produced by the thousands in Roman times, or the Chinese Jian ceramics, fired in giant dragon kilns during the Song dynasty (Dejoie et al. 2014a). Ancient ceramics are found on mostly all continents, each civilization having developed its own specificities in terms of shape, decoration or firing technique. Ceramics can be seen as cultural markers, and, owing to their resilience toward underground storage and time, a lot of sherds are available today for analytical studies. In this context, a review on the studies carried out on the glaze and slips of ancient ceramics, for which synchrotron radiation was used, is presented.

A different kind of material is the topic of the second contribution, also widely used in ancient times: iron-based materials. Metallic objects have been widely manufactured by ancient societies, to be used as tools, jewelry or weapons. Metallic objects have also been used as support materials, for example, as reinforcement in monuments. Iron-based materials are subject to corrosion, and through this contribution, the concept of long-term evolution of a material through the ages will be introduced. The study of corrosion involves knowledge of electrochemistry, and synchrotron radiation can be used to follow specific reactions, in situ. This illustrates how the study of Cultural Heritage materials is not simply limited to an ancient artifact, but can also lead to interesting research on a specific topic such as corrosion.

The concept of "support material" with great Cultural Heritage significance will be at the center of the third contribution, through a study of Roman concrete. Due to its specific properties, this material allowed quite complex monuments to be built and to survive over two millennia. In this contribution, a set of synchrotron-based techniques including X-ray fluorescence, X-ray powder microdiffraction and X-ray Laue microdiffraction was applied to the study of ancient concrete from Imperial Rome. The close examination of chemical and structural compositions of these concretes using synchrotron microprobe techniques allowed us to understand the chemical mechanisms behind the extraordinary resilience and longevity of these materials. Cultural Heritage materials can provide information about the long-lasting resistance of a material, something that cannot be reproduced easily in a laboratory. As a result, a material such as Roman concrete can also be attractive for modern applications, and this is an example showing how our past can be a source of inspiration to design new, long-lasting materials, following an archaeomimetic approach (Dejoie et al. 2014b). Specifically, roman concrete is currently actively studied by several researchers because of their durability and low carbon footprint, when compared to modern technologies based on Portland cement.

The last contribution opens the path toward a different field: biomineralization. Biomineralization, at the frontier of biology and materials science, refers to the process by which living organisms produce minerals. In the field of Cultural Heritage, materials obtained from a biomineralization process involve, among others, bones or ivory-based artefacts. The 3D structure of these materials is related to their origin and can serve as fingerprint of a particular species (e.g. mammoth tusk vs. modern elephant tusk), and their properties can be influenced by external factors, such as heating, weathering or burial conditions (Reiche and Chalmin 2008; Albéric et al. 2017). Biomineralization can sometimes lead to the long-term degradation of the artifact, but it can also be used as a strategy for conservation, for example, to preserve and reinforce stone-based materials (Marjadi 2016; Marvasi et al. 2020). Biomineralization leads to the formation of complex mineral architectures, with properties resulting from a multiscale organization. Understanding the mineralization process requires this organization to be probed from the nanoscale to the macroscale, and synchrotron-based techniques can be used to provide such multiscale information. The contribution will focus on the biomineralization process in sea urchins' spines, and how synchrotron techniques can help in deciphering calcium carbonate formation and stabilization.

1.4. Conclusion

The use of synchrotron radiation X-rays has strongly influenced many areas in materials science, including the field of Cultural Heritage materials and biominerals. Today, some efforts are still required to make synchrotron facilities a more routine solution for Culture Heritage and related fields communities. The first problem is practical: to access a synchrotron facility, a researcher has to submit a proposal which will be peer-reviewed. Not all proposals get funded and many beamlines are oversubscribed, so beamtime is not guaranteed. On the contrary, new access procedures such as the one mentioned earlier (BAG proposal at the ESRF) should ease and guarantee more regular access to beamtime to the Cultural Heritage community. There is also a lag time of up to six months or more between a proposal being submitted/accepted and the measurements being done, which may create some logistic problems (will the specimen be available for the beamtime? Are the measurements time sensitive?). Moreover, cultural heritage specimens are often unique and precious. Would the results justify the insurance cost of travelling the artifacts to the synchrotron radiation facility? Beam damage to the sample resulting from even short exposure to very intense X-rays is also a concern that needs to be carefully weighted in. Progress in lab-based X-ray technologies also made synchrotron radiation facilities not always the necessary tool for cultural heritage samples. Sometimes, long measurements in a readily accessible lab machine is preferable to very short measurements which may (or may not) happen in six months' time, especially when spatial or temporal resolution is not a critical issue! Cheap tabletop bright coherent X-ray source provided by a new generation of laser-driven plasma accelerators (Kneip et al. 2010) may also one day be a good alternative to synchrotron radiation facilities. For many researchers, in-situ measurements at the museum or directly on the excavation site may be preferred, and it is expected that portable X-ray fluorescence imaging or X-ray diffraction devices (Cuevas and Gravie 2011; Nakai and Abe 2012; Cuevas et al. 2015; Castaing et al. 2016) is becoming more commonplace. For the time being, however, synchrotron radiation continues to offer some sizeable advantages when it comes to spatial resolution and elemental sensitivity, compared to even the most efficient lab sources.

In this book, after an overview on the development of the use of synchrotron radiation for Cultural Heritage studies, we focus on two mapping strategies, through either X-ray absorption or X-ray diffraction and illustrate the enhanced capabilities provided by synchrotron radiation, surpassing what is generally possible with conventional lab-based techniques. Then, an overview of different studies carried out on a series of specific materials is presented, with a final chapter on the close-related field of biomineralization, highlighting how diverse the applications of synchrotron radiation for such complex and heterogeneous materials can be.

1.5. Acknowledgments

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