

Synchrotron Radiation InfraRed microspectroscopy and imaging in the characterization of archaeological materials and cultural heritage artefacts

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Fourier-transform infrared (FTIR) spectroscopy is a widespread and highly sensitive analytical method for the identification and characterization of a wide range of materials *via* their infrared (IR) absorption bands. Until now, the potential of IR microspectroscopy and imaging for the characterization of works of art or other objects of cultural heritage significance has been only partially exploited; in particular the use of the synchrotron radiation (SR) IR microprobe to study, at the micron scale, materials of interest for archaeological and cultural heritage studies has become popular only in the past decade.

One of the main requirements imposed on the studies of ancient and/or valuable materials is that the techniques applied must be non-destructive. In this scenario, SR-based FTIR methods are perfectly suitable. Moreover, IR spectroscopy and imaging are emerging techniques that combine the assets of IR in terms of molecular specificity with the unique properties of synchrotron light. SR-FTIR micro-spectroscopy offers great advantages over conventional methods because it provides a broader spectrum (down to THz) and higher spectral quality (signal/noise ratio) at the highest spatial resolution (diffraction limited). This is due to the high brilliance and collimation of SR-IR, while still being non-damaging to the investigated system. The unique SR-IR parameters are essential for the compositional analysis of the tiny, sub-millimetric samples characteristic of ancient materials, which are heterogeneous by nature, and with complex molecular distributions at extremely variable concentrations.

SR-FTIR spectroscopy and imaging can be applied successfully to the characterization of organic and inorganic materials *via* so-called IR fingerprinting, as well as for their compositional quantification. The range of materials investigated is very broad and encompasses painting materials, stones, glasses, ceramics, coatings on metals, paper and wooden materials, canvas or other textiles, organic colourants, resins, varnishes, cosmetics, and binding media such as glues, waxes, oils, *etc.* SR-IR-based methods can also be used to understand the historical technologies and to identify the raw materials used to produce archaeological artefacts and art objects, and to improve stabilization, conservation and restoration practices.

Selected applications of SR-FTIR methods are discussed with a special emphasis on the chemical and mineralogical characterization of ancient paintings, on the study of alteration and corrosion layers, and the separation and identification of pigments. New

perspectives offered by existing facilities and new developments in IR imaging and advanced vibrational spectroscopy that may broaden the variety of archaeological and historical materials that may be studied are outlined.

1. Introduction

Infrared spectroscopy was developed at the beginning of the 20th century for analytical purposes. From early on, IR spectroscopy was revealed to be a powerful analytical tool for identifying and quantifying molecules and molecular structures in solids, liquids and gases. Coblenz (1905) released the very first database of IR spectra with a table of the characteristic absorption bands for a series of materials. Used extensively by organic chemists since the 1950s, it was recognized as a fundamental method in Mineralogy and Earth sciences (Keller and Pickett, 1949, 1950), although the first comprehensive compilation of IR spectra of minerals was published much later (Farmer, 1974). In the late 1960s/early 1970s, the Fourier-Transform Infrared (FTIR) spectroscopy technique was established thanks to the feasibility of new interferometers and the availability of personal computers suitable to run the Fast Fourier-Transform (FFT) algorithm on-line. Since then, several reviews have been published on the application of IR spectroscopy in mineralogy, and a complete treatment of the infrared theory and aspects of instrumentation and methods became available (Hawthorne, 1988; Beran and Libowitzky, 2004).

The present chapter is intended to highlight aspects of infrared microanalysis and imaging that have been developed recently for the characterization of works of art or other objects of relevance to the cultural heritage and that use SR. Although the interest of SR in this field is mainly in the use of X-rays, in particular X-ray microanalysis, proposals focussing on the use of IR radiation have increased steadily. Several applications in the IR domain have been pointed out previously by Salvadó *et al.* (2005), Cotte *et al.* (2009b) and Bertrand *et al.* (2012a). The type of cultural heritage objects studied ranges from paintings to historical buildings, and involves a very broad range of materials. Among the subjects investigated are research into alteration and corrosion processes, and also the most recent theories and technologies concerning conservation and restoration. The specific goal of this chapter is to give an up-to-date perspective on the use of SR-IR microspectroscopy, which is a mature method applied extensively in studies requiring high spectral quality and ultimate spatial resolution on extremely small samples, *i.e.* $\sim 10\ \mu\text{m}$ or less. Finally the chapter covers the latest development of SR-IR imaging techniques as applied to the investigation of materials of archaeological and cultural heritage interest.

At present, operational SR facilities around the world offer dedicated lines for IR microspectroscopy and imaging. They host an ever-increasing number of multi-disciplinary users such as mineralogists, archaeologists and researchers working in cultural heritage. The interest in SR-IR has increased over the last 20 years because of the unique properties and advantages of this non-thermal source, *i.e.* a spectral emission following the universal curve for accelerators: an asymptotic behaviour at long wavelengths for relativistic electrons with energy greater than 0.5 GeV. Specifically: (1) SR is among the most broadband of sources, spanning from the far

IR (mm wavelengths) to hard X-rays; (2) SR emission is a ‘laser-like’ small diverging beam, still due to the relativistic emission of electrons, originating from submicron ‘wire of current’ of circulating electrons, unique features that allow us to overcome the source size-limitations of conventional ‘benchtop’ instruments, characterized by mm-wide sources and macroscopic angle of emission; and (3) SR emitted light is intrinsically linearly polarized in the plane of the orbit of the accelerated particles. The current rapid development of IR lasers must be noted. Such lasers offer great IR microscopy capability, either at a fixed wavelength (quantum cascade lasers and free electron lasers), or over a limited spectral range (*e.g.* super-continuum laser). However, the image quality (*e.g.* visual artefacts due to the laser light coherence), signal reproducibility and full IR bandwidth, *i.e.* full spectroscopy capability, are still under development.

As detailed below, the main advantage of SR-IR over conventional/blackbody sources is its brilliance, defined as the number of photons emitted per second per unit area and solid angle (horizontal and vertical) at the source (photons/sec/mm²/mrad²). A fundamental theorem in optics states that brilliance cannot be increased by any optical system (*e.g.* by lenses and mirrors). In practice, most photons from a small and collimated source like SR can be focused onto a small IR spot. On the other hand, a large-diverging IR source, *e.g.* a conventional blackbody, is very ineffective for illuminating microsamples. The gain in brilliance of an IR-SR source with respect to a conventional broadband source is from 100 to 1000 times when going from the near-to-visible IR (wavelength >700 nm) to the far-from-visible IR (wavelength <cm). The greatest advantage of SR over a conventional source is obtained using mid-IR microanalysis, plus exploiting the broadband character especially towards the far-IR for spectroscopy experiments. For imaging applications, the best performances are given by confocal microscopy (Minsky, 1988), an optical layout in which the optical objective (imaging light out) and the condenser (focusing light in) share the same focal spot size on the sample plane. This can be achieved *via* apertures placed at the conjugated foci, which enables the illuminated and detected areas of the sample to be the same size. The use of small apertures such as pinholes enables images with the greatest spatial resolution to be obtained, but at the cost of a low photon throughput *i.e.* reduced signal. The figure of merit for spectral quality is the signal-to-noise ratio (SNR), which must be sufficient for the spectral recognition of small spatial features in the image. The drawback of the use of pinholes or small rectangular apertures (<20 μm²) in IR microscopy is the dramatic degradation of the signal, hence the need for brilliant SR sources. It is worth remembering that IR light has longer wavelength than the visible, so the diffraction limit plays a bigger role in spatial resolution (theoretically $\delta x \geq \lambda/2$) for IR microscopy. In fact, the use of small apertures affects longer wavelength in the IR spectra to a greater extent. A practical rule of thumb for IR microscopy is that the slit size, *e.g.* $\delta x \approx 10 \mu\text{m}$, causes a cut-off in the spectrum at a comparable wavelength scale, *i.e.* $\lambda \approx 10 \mu\text{m}$.

The recent availability of mid-IR range multi-pixel detectors, equivalent to visible spectral range charge-coupled devices (CCDs) and known as Focal-Plane-Array (FPA), has revolutionized the use of FTIR imaging. These devices consist of a bidimensional

array of small IR detectors (pixels) a few tens of microns in pitch. They allow the acquisition of thousands of IR spectra simultaneously, generating mid-IR images at high spatial sampling in a short time (\sim minutes). The optical system of an IR microscope (Fig. 1) equipped with a FPA is an ‘apertureless’ imaging system, the ultimate spatial resolution of which is a factor two less than in confocal microscopes. Nevertheless, FPA sensitivity and read-out speed enable different imaging, namely oversampling specimens at the micron scale or providing a large field of view. Massive and fast data collection within several minutes is thus achieved (Colarusso *et al.*, 1998; Bhargava and Levin, 2001, 2007; Petibois *et al.*, 2010).

For Earth science materials, SR-IR has been applied successfully in studies which require either an improved spatial resolution, *e.g.* for fine-grained synthetic crystals, or high brilliance, such as in high-pressure (HP) studies using diamond-anvil cells (Scott *et al.*, 2007; Noguchi *et al.*, 2012). The new imaging capabilities of FTIR microscopes have also been used to address features such as zoning of volatile species across samples or possible conformational changes of structurally bound carbon molecular species during crystal growth, all features which are barely accessible using standard micro-analytical techniques. Recent studies have also explored the use of FTIR imaging to monitor processes in real time (Della Ventura *et al.*, 2010).

2. Basics of Fourier Transform InfraRed spectroscopy

Depending on convenience, electromagnetic (e.m.) radiation can be thought of either as a wave propagating and transporting energy and momentum, or as a flux of photons, *i.e.* massless particles travelling in space and absorbed or scattered by materials. The

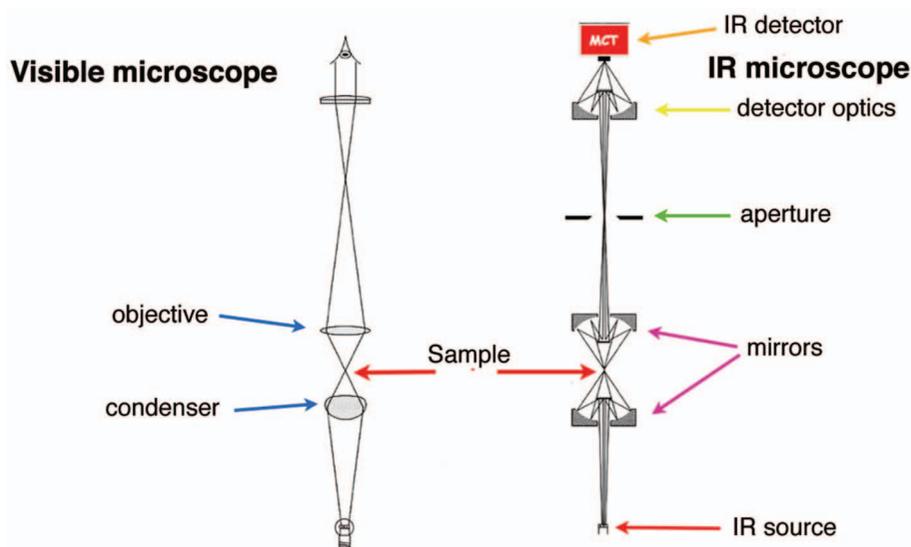


Figure 1. Comparison of the layout of an IR microscope (right) with that of a visible light microscope (left).

spectrum of e.m. radiation is the range of the wavelengths it covers, or the energy associated with photons; in practice, it extends from km- to cm-long wavelengths for radio-/microwaves, to mm- to μm -long for IR, or below $1 \mu\text{m}$ for the visible “rainbow” and the UV, up to Ångstrom-size wavelengths for X-rays (see Fig. 2a). Due to diffraction limit implications, this length of scale is crucial for microscopy purpose. The Abbe diffraction limit sets the greatest spatial resolution achievable at $\lambda/2$. Thus in the visible, sub-micron spatial resolution is optically possible, but such a resolution is not attained in the IR range.

On the other hand, the energy associated with photons dictates the interaction regime that the e.m. radiation can probe. X-rays and UV are ionizing radiations spanning energies above 10 eV, which means that they are capable of interacting with the atomic and electronic structure of matter. Together with visible light, the energy of which is a few eV, X-rays and UV radiation can induce sample luminescence and/or damaging/bleaching. IR photons in contrast are in the sub-eV regime, *i.e.* so soft to be well below any damaging threshold, but capable of exciting molecular oscillations within solids. From the fundamental equation between photon energy and light wavelength $E = hc/\lambda$, a rule of thumb can be obtained: $\lambda E = 12400 [\mu\text{m meV}]$ or equivalently $\lambda = 100 \mu\text{m} \leftrightarrow E = 124 \text{ meV}$.

Specifically, the IR domain is generally divided into three parts named with reference to the ‘spectral distance’ from the visible: near-IR (wavelength 0.7 to $2.5 \mu\text{m}$ or from ~ 1800 to 500 meV), mid-IR (2.5 to $50 \mu\text{m}$ or from ~ 500 to 25 meV), and far-IR ($>50 \mu\text{m}$ or $< 25 \text{ meV}$). Historically, the way in which IR spectra were drawn was *vs.* wavenumber, the latter defined as the inverse of the wavelength in units of cm^{-1} . For an easier conversion, a practical rule correlates wavelength and frequency: $\lambda = 100 \mu\text{m} \leftrightarrow \nu = 100 \text{ cm}^{-1}$. Nowadays, it is common to refer to the THz region, which is the far IR with frequency from 0.3 to 3 THz. By rewriting the fundamental equation $c = \lambda * \omega$, where c is the speed of light, the equivalence $1 \text{ THz} \leftrightarrow 300 \mu\text{m} (\sim 4 \text{ meV})$ is obtained.

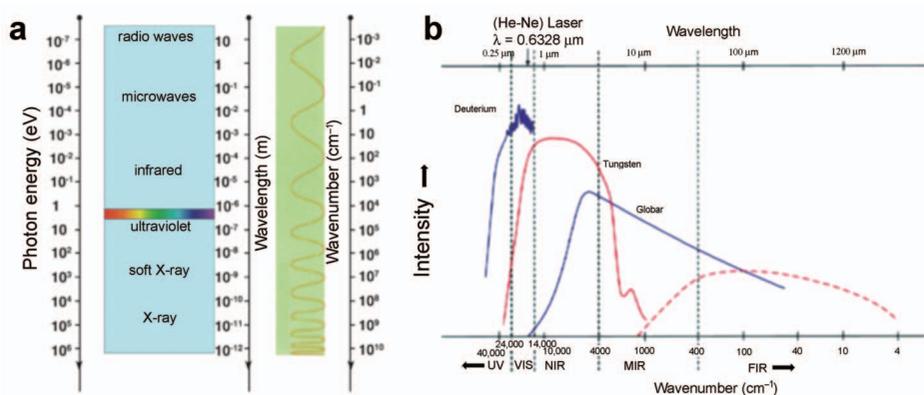


Figure 2. (a) The regions of the e.m. spectrum *vs.* energy, wavelength and wavenumber covered by a synchrotron radiation source; (b) the various conventional sources necessary to cover the IR domain from the THz to the NIR and visible to UV regions.

Lamps based on the incandescence of electrically heated filaments are still the most used conventional sources (Fig. 2b). They rely on the so-called e.m. emission of a blackbody: a perfect all-wavelength absorbing material which gives a universal spectrum as a function of its temperature only. A blackbody is a particularly powerful, isotropic and homogeneous source of visible-to-IR light useful for most purposes of spectroscopic analysis of macroscopic samples. In the IR field this is referred to as global, *i.e.* a few mm element heated around or above 1000 K to emit a bell shape spectrum conveniently peaked at $\sim 2.9 \mu\text{m}$ or below according to the Wien law, *i.e.* in the mid-IR region. As a variation, spectral emission from light bulbs ($T \approx 2000 \text{ K}$) is used for near-IR, and Mg lamps for the gas emission in UV and far-IR due to light Doppler shift from N_2 buffer gas.

The basis of absorption spectroscopy lies in the idea of characterizing an unknown sample by measuring the light loss across it. The ratio of the light intensity measured after (I) and before (I_0) an illuminated sample is its transmission ($T = I/I_0$), and its transmission spectrum, $T(\lambda)$, is its plot as a function of wavelength. Lambert-Beer's law states that the intensity of an electromagnetic wave penetrating a material falls off exponentially with distance from the surface: $I/I_0 = e^{-\alpha(\lambda)L}$, where $\alpha(\lambda)$ (units of m^{-1} or submultiples) is the absorption coefficient of the specific material and L the sample thickness. The absorbance A , a dimensionless quantity sometimes called optical density is a property of the specific sample calculated as the inverse of transmittance in a log scale: $A = \log(1/T)$. Again, the absorbance spectrum $A(\lambda)$ is plotted *vs.* wavelength.

Comparison of these definitions shows that $A = \alpha(\lambda)L/2.303$. Also useful to note is that the penetration coefficient is the reciprocal of the absorption coefficient, that is the thickness of material for which the amount of light has reduced to $1/e$ ($T \approx 37\%$). An absorbance equal to one means that the amount of light has reduced by 10 times across the sample; an absorbance of 0.1 means $\sim 80\%$ transmission. Because the linearity range of most detectors used in the IR region is physically limited, reliable spectroscopy measurements are generally possible for samples with absorbance between 2 and 0.01 (or transmission between 1% and 98%). Above and below such limits, IR spectroscopic data are no longer quantitatively accurate.

At present, the most common spectrometer for IR spectroscopy is the Michelson interferometer (Fig. 3). In this system the IR radiation from a source goes through the instrument pupil and is split 50/50 into two beams by a semi-reflecting mirror called a beamsplitter. A series of mirrors in a 'cross' configuration makes the two beams recombine into one: this is

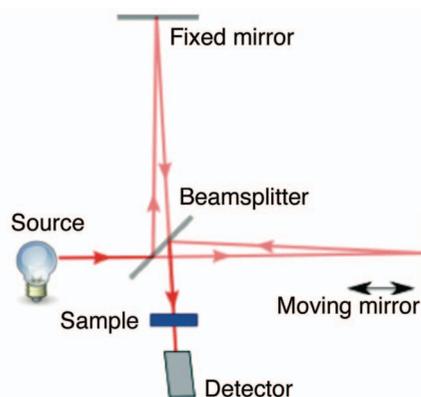


Figure 3. The optical layout with main optical elements of a Michelson interferometer.

brought onto a detector after having been through the sample. In one of the two arms of the 'cross' a moving mirror modulates continuously the radiation path for all the different wavelengths passing through the interferometer. The basic idea is that reflected and transmitted beams split by the beamsplitter are recombined to produce positive/negative interference: this happens for each wavelength travelling a distance equal to an even/odd multiple of $\lambda/2$.

All wavelengths interfere constructively for equal paths (centre burst), but their intensities modulate as a decreasing oscillation for longer path differences. Such a recorded signal is called the interferogram, and it represents the light output as a function of the mirror position, which is correlated to each wavelength IR intensity. It can be demonstrated that the interferogram is the Fourier Transform (FT) of the IR spectrum. By Fast Fourier Transform (FFT) algorithm, data are processed in real time and transformed in a spectrum where the absorbance of the sample is plotted vs. wavelength. As a consequence of the FT method, the relation between mirror path and spectral resolution (the minimal measurable separation between two close spectral peaks) means that the resolution expressed as wavenumber (cm^{-1}) is the inverse of the mirror path (cm). Compared to a dispersive instrument, the complexity of a FTIR spectrometer is largely compensated by a greater advantage, namely that the information in the entire frequency range is collected simultaneously, improving both acquisition speed and signal-to-noise ratio (SNR). This is the multiplex or Fellgett's advantage. The other merit of the interferometer is its high throughput, also called the Jacquinot's advantage. In fact, the whole beam from the source is used in an interferometer, while in any dispersive instrument slits are necessary to define the bandwidth, at the cost of less light being detected.

In condensed matter, any molecules can absorb e.m. radiation by reaching an excited vibrational state (transition in the IR), or an electronic state (transition in the UV or X-ray). Physically, the energy levels are quantized; therefore, the light absorption by a molecule takes place only for photons of energy corresponding to the gap from the ground to an excited state. Semi-classically, the criterion for IR absorption is the presence of, or change in, electric dipole moment in a molecule. Absorption occurs when there is a match in frequency between the radiation and the molecule harmonic oscillation. Molecules without a permanent/induced dipole moment cannot absorb IR radiation.

In polyatomic molecules and in a condensed phase, vibrational motions, distinguished by stretching (*i.e.* a change in the interatomic distances), and bending modes (*i.e.* a change in the angle between two bonds) provide the main IR evidence. A molecule with a number of atoms, N has $3N$ degrees of freedom in a system of Cartesian coordinates. For a generic molecule, 3 of these degrees of freedom are rotational and 3 translational; the number of fundamental vibrations or IR bands is thus $(3N - 6)$. In a linear molecule, there are only 2 rotational degrees of freedom: the fundamental modes are thus $(3N - 5)$. For example H_2O is a non-linear molecule composed of 3 atoms, thus it has 3 fundamental modes in the IR, namely asymmetric and symmetric stretching plus bending vibrations. CO_2 is linear molecule thus with 4 fundamental modes. Of the

2 stretching modes, the symmetric one is not IR active because there is no change in dipole moment. The other 2 bending modes are degenerate in energy so that they merge into one band only.

IR spectroscopy is actually the most routine technique employed in identifying molecular/chemical compounds based on the presence of different functional groups *via* their absorption bands. In general for complex molecules their recognition by vibrational spectroscopy is made *via* the so-called mid-IR fingerprint, *i.e.* using the part of the spectrum below 2000 cm^{-1} , mostly associated with the bending modes of the functional groups, where IR bands are affected by the surrounding atoms of the molecule structure. At a first approximation, the interpretation of stretching modes in an IR spectrum can be done with reference to the harmonic oscillator strength and reduced masses, so the C–C mode is $\sqrt{2}$ lower in frequency than the C=C one, while the C–H mode is $\sqrt{3}$ higher in frequency because of the reduced mass change carbon to hydrogen, *etc.*

In terms of the actual acquisition mode of the spectra, transmission analysis in the IR regime is done by first measuring the background, *e.g.* on the sample support to get the I_0 , and then on the sample, to obtain I , at any wavelength. Then Transmittance (and Absorption) is calculated as explained above. IR opaque samples can sometimes be measured in specular reflectance if the specimen is optically polished: *via* the Kramer-Kronig relations linking refractive index and absorbance, the transmission spectrum can be calculated by most acquisition software, while the inverse is non-trivial. Thin samples can be measured if deposited on a reflective substrate, and the method is called transreflectance. The Attenuated Total Reflection (ATR) method is used for semi-infinite samples. Here the IR light illuminates a sample through a high refractive index crystal such as Ge, Si or diamond, which is placed in contact with the material to be analyzed. The incoming beam is at a small angle with respect to the crystal–sample surface, so that it is below the critical angle of total reflection. At the interface some light leaks into the sample; if the material absorbs at some wavelengths, then the reflected light is modulated accordingly, and an IR spectrum is produced. This method can also be applied in IR microscopy using all-mirror based objectives and condenser in the Schwarzschild geometry, also known as Cassegrain optics (Fig. 4).

3. Synchrotron Radiation and IR microanalysis, principles and advantages

Synchrotron radiation exhibits several unique properties as a photon source: (1) high brilliance; (2) broadband and continuous intensity distribution over the entire e.m. spectrum; (3) a high degree of polarization; (4) ultrafast time structure; and (5) high stability. Historically, the IR SR emission first used was the classical bending magnet (BM) radiation, which is characterized by the broadest IR spectrum coverage extending from microwaves to the IR domain up to X-rays (Hofmann, 2004). More recently, e.m. radiation emitted by electrons travelling through the fringing magnetic field of a BM has been exploited; this takes the name ‘edge radiation’ at entrance/exit of a bending magnet. Such a source is limited to the lower energy of the spectrum, *i.e.* visible to IR,

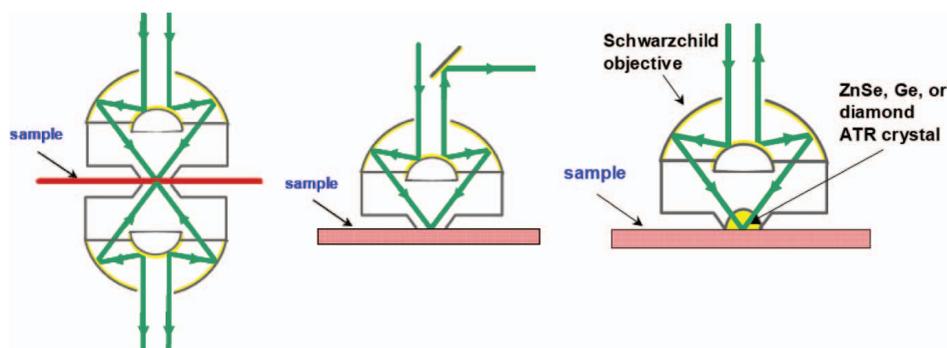


Figure 4. Optical layout of Cassegrain objective and condenser systems as used in transmission (left), reflection (centre) and micro Attenuated Total Reflection (right) geometry.

and in practical terms is comparable to the standard BM radiation for IR purposes, with a flux benefit towards the longer wavelengths spectrum.

The most exploited advantage of synchrotron radiation is its broadband brilliance. Rather large collection angles are required at a beamline ‘front-end’ to extract long wavelengths – such as the IR – out of bending magnet sources. This is because the intrinsic light divergence increases up to several orders of magnitude from the characteristic synchrotron divergence $\theta \sim 1/\gamma$ (γ , relativistic factor for electrons) for X-rays at critical energy. On the contrary, long-wavelength radiation emitted as edge radiation has a significantly smaller opening angle than standard BM radiation.

The history of SR applications in the long wavelength region and in particular the IR is more recent than that for UV and X-rays (Marcelli and Cinque, 2011). In fact, SR sources are some orders of magnitude more brilliant than a conventional black body source with the same spectral range (Fig. 5)¹. If a highly brilliant source is not a priority for standard spectroscopic measurement, it becomes mandatory in microscopy or microanalysis where a spot size down to the diffraction limit is highly desired in many applications. In fact, the signal and spectral quality decrease drastically if apertures are reduced to define a smaller beam for the sake of lateral resolution (for example, see Fig. 6 for organic matter).

The use of IR microscopes coupled to SR sources provides outstanding results because the high brilliance of this source allows the microscope apertures to be reduced to the diffraction limit, *i.e.* down to a few microns in the mid-IR region (Carr, 2001). The electrons in the storage ring do not have a continuous distribution around the orbit in a circular accelerator but are stored and travel in bunches, thus the resulting emission has a time structure. The SR is indeed emitted as light pulses with duration and separation characteristic of each ring, typically ranging from tens of psec to tens of nsec. This is another interesting characteristic of this source for users interested in time-resolved experiments. An additional and key feature of SR is its polarization. Owing to

¹ We are not discussing the use of IR laser sources because they are not yet standardized as routine instruments for FTIR.

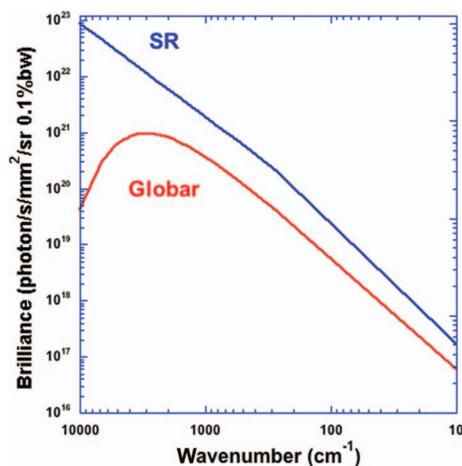


Figure 5. Comparison of the calculated brilliance of a 3 GeV synchrotron radiation bending magnet source at 1.4 T vs. a conventional source.

Experimental observations indicate that values up to 80% of circularly polarized light can be obtained using a set of slit that selects ~50% (upper or lower part of SR fan) of the total flux available (Cestelli Guidi *et al.*, 2005).

SR emission geometry, BM radiation is linearly polarized in the orbital plane. Since the early pioneering work in the visible region, studies performed both in the UV and X-ray regions demonstrated that when light is observed above or below the orbit plane, the radiation is circularly polarized. The polarization properties of the SR at long wavelengths are very interesting for many applications, in particular in the far-IR region. By placing a slit on the exit port, one can, in principle, select the desired degree of circular polarization and the flux of the emitted radiation. About polarization, we may define three polarization indices, of which two are more important: the linear and the circular polarization.

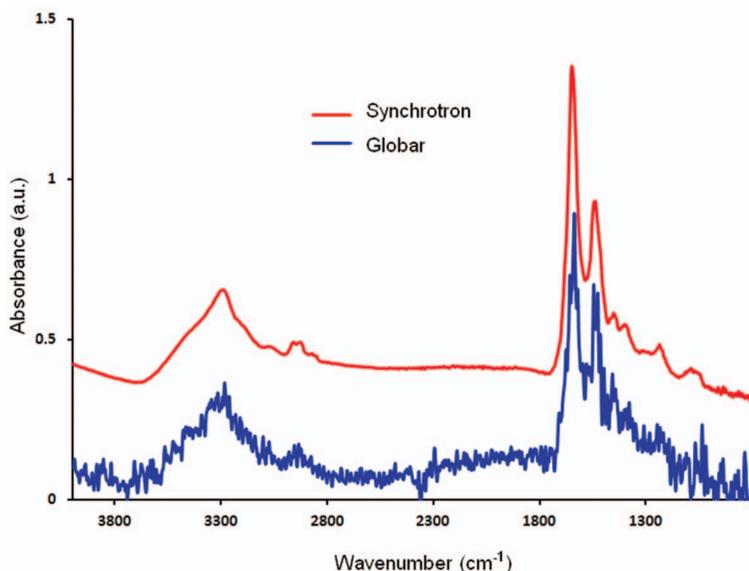


Figure 6. Comparison of the IR spectral quality obtained on an organic microsample by a conventional source (lower) and a SR-IR source (upper) both over the same area (slit size $5 \mu\text{m} \times 5 \mu\text{m}$) and in 30 s. The absorbance curves are in scale and shifted for clarity. The figure of merit SNR (rms) is <200 for the Globar (blue) and >5000 for the SR (red), respectively.

In SR-IR beamlines, commercial FTIR benches and microscopes are generally installed, and the SR replaces only the conventional source. The IR beam is focused in the upper part of the microscope (Fig. 1) and is projected onto the sample plane by a reflective objective; the slit dimensions determine the microbeam size, and the relations between spectral cut-off and resolution in these conditions have been discussed previously. More details can be found in the paper by Marcelli and Cinque (2011).

The goal of FTIR microscopy is to attain the best spatial resolution at the sample location, while exploiting the typical sensitivity of IR spectroscopy to molecular composition. The concept of spatial resolution in IR imaging is not an absolute parameter for non-monochromatic systems: it is limited by diffraction and affected by both the optical design, *e.g.* objectives and slits, and the final contrast achieved (Levin and Bhargava, 2005; Levenson *et al.*, 2006, Bhargava and Levin, 2007). According to Rayleigh's criterion, two points can be separated *via* a microscope when the central maximum of the diffraction pattern of the first (*e.g.* due to a plane e.m. wave encountering an infinitesimal pinhole in a screen) is at a distance greater than the first minimum of the Airy disk of the second. This is shown in the upper right part of Fig. 7.

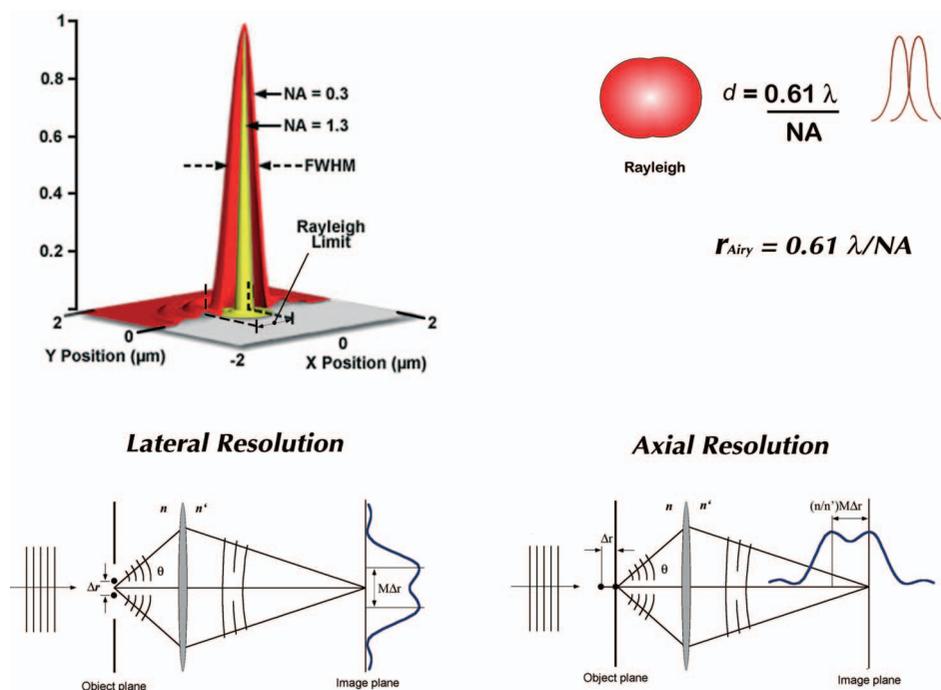


Figure 7. (Upper, left) Comparison of the Point Spread Function (PSF) between two optical systems with different Numerical Apertures (NA). (Upper, right) The Rayleigh criterion where two points can be resolved spatially if the central maximum of the Airy disc of the first is at a distance of one radius ($0.61 \lambda / NA$) from the second. (Lower) Comparison of spatial lateral (left) and axial (right) resolution for confocal and widefield microscopy.

When a point source of monochromatic radiation goes through the microscope optics, the Airy pattern is observed at the beam focus, *e.g.* onto the sample. The central circular area of the Airy disc, known as the point spread function in 2D, in Fig. 7 is characterized by a radius $r = 0.61 * (\lambda/NA)$, where λ is the wavelength and NA is the numerical aperture of the microscope. If we consider a standard optical microscope illuminating a large sample region, the ultimate resolution can be achieved by an ‘optical system’ made by the objective optics and the optical camera. Similarly, in an IR microscope using an IR area-detector, *i.e.* a focal-plane array (FPA) detector, the spatial resolution is determined by the magnification of the optical system, with the size of the individual pixel of the detector also being a relevant parameter (Miller and Smith, 2005).

In a microscope, the field of view (FOV) can be reduced by using a field stop, *e.g.* an aperture placed at an intermediate focal point; in this case, the spatial resolution is determined by the fraction of light from each point of the specimen that reaches the detector, *i.e.* its sensitivity pattern. As outlined above, if we reduce the illuminated region while maintaining an homogeneous illumination, then the spatial resolution is a function of the number of photons that illuminate the small selected region of the specimen. To probe this small region of a specimen, the microscope must illuminate it and simultaneously detect the light. A confocal microscope has identical apertures for both the illumination and detection systems. It achieves the ultimate spatial resolution by reducing to the same size both the illuminated region and the region to be detected. An image of the specimen under analysis can then be collected, although with much longer times, by rastering the sample through the focus of the confocal microscope. In this case, standard IR single-element detectors, typically with areas of $250 \mu\text{m} \times 250 \mu\text{m}$, are not suitable for work at high spatial resolution. In fact, the effective projection of a detector pixel size onto a sample by a standard IR objective (*e.g.* $15 \times$, plus the microscope internal optics) can be one order of magnitude larger than the IR wavelength limit (*e.g.* $\sim 170 \mu\text{m} \times 170 \mu\text{m}$), *i.e.* far beyond the minimum diffraction limit. Moreover, their intrinsic noise is proportional to the dimension of the detector (and the SNR proportional to $\sqrt{\text{area}}$), which is a real bottleneck for spectral quality. In practice, smaller IR detectors (commercially available $<100 \mu\text{m} \times 100 \mu\text{m}$) are both less noisy and better match the SR beam size for best performances in IR microscopy.

In contrast to confocal microscopes with single-element detectors, the combination of a SR source with a two-dimensional FPA detector is an alternative way to take advantage of SR-IR brilliance for imaging and time-resolved experiments. Using IR area-detectors FTIR spectra can be collected simultaneously over large areas (generally less than hundreds of μm^2) depending on the magnification (generally, above $15 \times$). IR snapshots containing hundreds of points are obtained within minutes, to be compared with acquisition times in the range of hours typically required by single-element detector mapping. Although in principle a sub-second timescale is necessary for a single FTIR spectrum, the raster scan method of IR mapping gives intrinsically the highest spatial resolution but is much slower in acquisition time. Ideally, the wide IR

fan available from a high-current synchrotron radiation facility can be shaped to illuminate a limited number of pixels of a FPA detector, and the brilliance advantage per small pixel size can increase the SNR ratio of the IR image by a high contrast (Petibois *et al.*, 2010). For these reasons, SR-IR coupling with FPAs is being developed increasingly especially for biological studies; in contrast, very few studies of materials of interest to Earth Science have been done so far in spite of the enormous potential. Recently, a synchrotron-based multiple-beam FTIR chemical imaging beamline was used in the SR Madison facility (USA), providing new opportunities to examine samples of interest to the cultural heritage community (Unger *et al.*, 2013).

Focusing on resolution, great emphasis is usually placed on the lateral resolution. However, to interpret an image it is also important to consider the axial (or in-depth) resolution, *i.e.* the axial resolving power of the objective measured along the optical axis. Similar to lateral resolution, axial resolution (Fig. 7) depends on the numerical aperture (NA) of the objective (Inoué, 1995; Born and Wolf, 1997). Lateral and axial spatial resolution for a confocal microscope are better by $\sim 50\%$ and $\sim 30\%$, respectively, compared to a corresponding microscope working with a wide-field illumination as shown in Fig. 7. A large NA improves both the lateral and axial spatial resolution of the microscope, although the NA of the microscope objective is much more effective for the axial resolution ($\sim \lambda/NA^2$) than the lateral one ($\sim \lambda/NA$). Knowledge of the axial resolution is fundamental for performing ‘optical sectioning’, a technique which enables a three-dimensional reconstruction of a sample *via* non-destructive depth profiling, *i.e.* collecting images as the focus is moved deeper into the sample. This method offers clear advantages for a non-destructive sample analysis such as that required for precious artefacts.

There are essentially three possible experimental set-ups in FTIR microscopy: (1) point analysis in a confocal layout; (2) FTIR mapping done by integrating the signal from successive locations of the specimen surface; and (3) FTIR imaging, performed with bi-dimensional arrays such as focal plane array (FPA) detectors. The main advantage of observing an entire field of view at the same time allows spatially-resolved spectroscopy of large and multi-phase samples.

Single-spot analysis can be done in both transmission and reflection modes. The spot size at the sample under the microscope illuminates images which are 30–100 μm across using a conventional source, which can be reduced to 3–20 μm across by using a SR source. To characterize the spatial distribution of an absorber across a sample, a standard practice is to isolate a small area of interest using apertures placed before or after (or both) the sample and then collect several spectra along traverses. Guilhaumou *et al.* (1998) presented the first application of this technique using SR-FTIR microscopy to monitor the evolution of the OH peak while using a small aperture.

In the FTIR-mapping mode the IR spectrum is measured at each in-plane point and then peak heights, peak areas, the integer performed in a defined spectral region or other criteria are used to visualize the distribution of the target molecule. This experimental set-up can be coupled to a confocal-like set-up to achieve good statistics and a high SNR. However, the method requires collection of a large number of single spectra and

reliable movement of the sample on the stage; consequently, the acquisition time for collecting data from large areas, *e.g.* a few mm², is up to several hours. In the FPA-imaging mode, the whole image is obtained in a single data collection thanks to a multichannel detection, similar to recording images with CCDs in optical microscopy. The number of pixels (the detectors) and their effective size will depend on the FPA type used. Typical arrays, designed for conventional sources, range from the 64 × 64 channels, providing 4096 individual spectra, to 256 × 256 or 1024 × 1024 channels allowing imaging of much larger areas. However, these detectors are not optimized to match a SR source that, because of its brilliance, may illuminate effectively only a limited portion of a bi-dimensional device (Petibois *et al.*, 2010). Such arrays are coupled with 15 × or 36 × objectives, so that with a single image up to few mm² in size, a single pixel corresponds to a physical dimension in the range 2.6 to 1.1 μm. Although FTIR imaging has evolved rapidly as a tool in biological and biochemical sciences, very few applications have so far been published in Earth Sciences (Della Ventura *et al.*, 2010, 2014).

4. General applications of IR microspectroscopy to materials of historical interest

SR-IR applications cover the full field of the Earth Sciences at different scales, including crystals and minerals in natural rocks (rocks may contain amorphous phases but minerals are crystalline, although not always in crystal shape), assemblages of various solid phases, and even glasses. Minerals are often twinned or contain fluid inclusions. The analysis of inclusions such as gas and liquid molecules like H₂O/OH in solids has been applied to nominally anhydrous minerals, similar to the occurrence of H, C and N-based molecules in minerals and interplanetary dust particles, and in some cases also in high-pressure studies. Applications in cultural heritage have become more and more frequent in the last decade. Complementary to other techniques, vibrational spectroscopy – either IR or Raman – is used widely in the Earth Sciences to characterize thin sections of geological materials with a spatial resolution that can reach the micron scale. Both methods have high molecular specificity. IR has the advantage of greater sensitivity and is totally non-destructive; Raman can provide higher lateral and longitudinal resolution but requires significant laser power to be applied to the specimen to obtain a good spectral quality².

Guilhamou *et al.* (1998) and Bantignies *et al.* (1998) were among the very first to explore the potentiality of SR-FTIR microspectrometry for such studies. In particular, Guilhaumou *et al.* (1998) addressed the analysis of hydrocarbon-rich fluid inclusions in siliceous diagenetic materials, aimed at constraining petroleum formation and migration. SR-IR microspectroscopy has also been applied in archaeology,

² An excellent review paper on microRaman outlining key applications of the technique to Earth Sciences including a good reference catalogue of Raman spectra for representative minerals was published by Gillet (2006).

archaeometry and in the study of cultural heritage materials because it is a highly sensitive, reliable and non-destructive analytical tool. Most important are studies of ancient painting materials, which are typically multi-layered and structurally heterogeneous, and can contain various fine-grained mixtures of minerals, pigments and binding media. Salvadó *et al.* (2005) neatly outlined three experiments aimed at demonstrating the importance of synchrotron-based IR microanalysis and sample preparation in the cultural heritage field. More specifically, the characterization of mineral pigments present in polychromatic stucco used for the wall paintings in a Roman villa was made on a micrometric fragment spread in a diamond cell to obtain a thin section suitable for transmission. The same preparation method was used to reveal the evolution in medieval painting techniques, namely the change of the organic binding media from tempera to oil that occurred between the Gothic and the Renaissance periods. In this case, a further method was used, which required measurements in reflection mode on a polished surface after the fragment was embedded in a plastic material and cut into slices. Finally, the determination of the corrosion of a Corinthian-type helmet by direct IR measurement in reflection on the surface of this single bronze piece: this again revealed the presence of a thin protective organic coating on the metal (Pantos *et al.*, 2005).

In situ characterization of the various components of these materials is essential to extract information about the techniques used during manufacturing and the origin of the materials used, as well as to design appropriate restoration procedures. A combination of X-ray diffraction/absorption and SR-FTIR spectroscopy has provided considerable advancements in these studies. For an overview of such combination the reader may refer to Cotte *et al.* (2009a). Notable investigations involved the analysis of Romanesque wall paintings from Unha (Val d'Aran) (Salvadó *et al.*, 2008) and the study of the alteration of silver foils in medieval painting from the Museu Nacional d'Art de Catalunya, Barcelona (Salvadó *et al.*, 2011).

Another field of application is the characterization of historical findings, as well as prehistoric artefacts of interest. For example, lithic artefacts were frequently used in prehistory, and deciphering the origin of the raw material provides information on the trade and migration of the first human societies. Bernardini *et al.* (2011a,b) used SR-based microFTIR directly on specific points of polished thin sections of serpentinitic rocks and specimens of prehistoric axes in order to identify the different polytypes of serpentine minerals. Notably, IR microspectroscopy was performed in reflection mode, *i.e.* without a need to sample the objects. The use of a synchrotron radiation source was a prerequisite because it provides both the spatial resolution and the spectral quality needed for the discrimination of different occurrences of serpentine minerals intimately intergrown with other sheet silicates. In practice, spectra were measured on features <20 µm long, or on poorly reflecting material like most real samples, which gave diluted signals requiring SR microFTIR to achieve a signal-to-noise ratio higher by several orders of magnitude than those obtained with conventional systems.

A fundamental issue underlining the analysis of multi-layered or multi-phase samples by imaging or microscopy is sample preparation. Cotte *et al.* (2009b) reviewed

different procedures in the particular context of synchrotron-based microanalysis concerning both IR and X-rays.

Besides the use of transmission and reflection modes in IR spectroscopy on thin samples or polished specimens respectively, micro Attenuated Total Reflection (ATR) is a valid alternative, which may be applied to many samples either non-reflective, or optically very dense. In the first two modes, spatial resolution is limited by optical diffraction to practically $\sim\lambda$, which can hardly be achieved or useful in terms of the SNR ratio considerations unless a SR source is used. Micro-ATR imaging offers better spatial resolution (up to a factor of 2–4 times greater) because of the change in refractive index between the ZnSe or Ge-crystal element and the sample matrix, which, in practice, eliminates any sample preparation. Goodall *et al.* (2008) used a micro-ATR device to characterize Mayan wall paints from an ancient chamber with the objective of identifying the mineral phases in the paint and stucco. FTIR spectra identified successfully the various mineral components, and the greater spatial resolution given by the micro-ATR allowed identification, spatially, of the different particles in the paint: hematite and silicate particles with minor amounts of calcite, magnetite particles in a sub-micrometer hematite and a calcite matrix – also in the underlying stucco – *i.e.* a combination of calcite with fine carbon particles. The use of micro-ATR in combination with a FPA detector is of particular importance; in fact, IR images allowed the authors to decipher the orientation and morphology of individual grains.

5. Selected examples of IR imaging in archaeology and cultural heritage

The specialist use of synchrotron radiation to probe cultural heritage and archaeological specimens dates back ~ 20 years. In terms of the synchrotron techniques used, most of them were X-ray-based methods, including both spectroscopy (X-ray fluorescence/absorption), and diffraction (crystalline and small angle scattering) (Bertrand *et al.*, 2012a). In this context, synchrotron-based FTIR microanalysis started more recently and immediately for microscopy/imaging purposes. By exploiting the high sensitivity of IR to low-Z elements of interest in mineralogy, which are difficult to detect using X-ray analysis, IR high specificity to functional groups in organic molecules for chemical analysis is an invaluable asset.

The following choice of IR examples is not to be considered exhaustive, but rather a series of significant examples taken from recent works published in the field, with the purpose of highlighting the state of the art of the technique and the breadth of applications. The range of materials probed is very diverse and includes painting fragments, bones, pottery and ceramics, metal and stone artefacts, wooden materials, as well as organic-inorganic mixtures in ancient plaster and cosmetics, thus reflecting the large variety and complexity of archaeological and cultural heritage studies.

A first case study showing both the non-destructive character of SR-based FTIR microscopy and its high sensitivity concerns microanalysis of the patina deposited on Dogon statuettes (Mazel *et al.*, 2008). The Dogon are among the most studied ethnic groups in West Africa. Since the beginning of the 20th century, many ethnographical

missions have been undertaken to study their beliefs and culture. These patinas were formed during religious and ritual ceremonies, and the anthropomorphic statuettes from the Dogon culture are well known examples of this kind of practice. For the purpose of better understanding details of the ceremonial practices throughout the centuries (the samples span the 15th to 17th centuries), the underlying idea was to extract unequivocal information about the original constituents and the method of deposition of these patinas. After preparation using ultra-microtomy of embedded samples, different chemical IR images led to the identification of minerals (clays, quartz and calcium carbonate) and organic products, as well as mapping their spatial distribution (*e.g.* proteins, starch, lipids as shown in Fig. 8). For some of these artefacts, the significant quantity of minerals and the lack of stratigraphy, as revealed by IR maps, suggested that the patina was deposited all at once, according to different recipes. The mineral portion consists mostly of quartz and alumina-silicates, although kaolinite was also identified in some samples. This composition corresponds to minerals that can be found readily in the Dogon area. However, differences suggest the existence of a variety of rituals more extensive than that described by the ethnologists.

A second example concerning the use of minerals in prehistory is the study of serpentinite stone, as the most frequently used raw material to produce polished lithic artefacts (Bernardini *et al.*, 2011a). Bernardini and coworkers characterized axes using a range of mineralogical and chemical techniques in order to locate the primary outcrops of their raw materials, and related areas of secondary exploitation. The evolution of mineral components in stone axes during the Neolithic to Copper Age transition in the so-called Caput Adriae (northeastern Italy, central and western Slovenia and northwestern Croatia) is of interest because it is linked to the development of early European metallurgy. Serpentinite shaft-hole axes in this regional archaeological context have a rounded, irregular shape, suggesting that the raw material came mainly from secondary deposits, thus the motivation for the identification of primary and secondary sources. Several conventional analytical techniques can identify the different serpentine minerals, but their application generally requires a powdered sample, which means damaging artefacts. The use of spatially resolved techniques is also a must in order to address sample non-homogeneity. SR-FTIR spectroscopy is ideal in many respects; it is a spatially

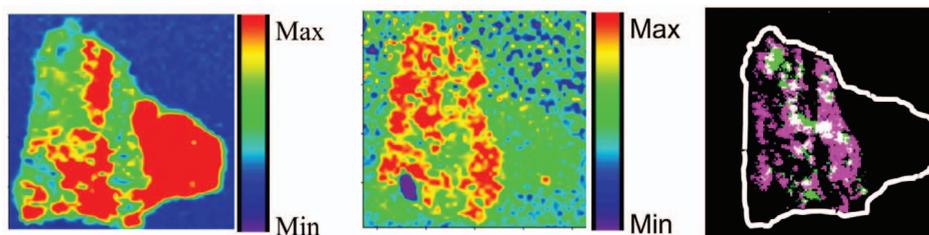


Figure 8. SR-IR images of the sample of a Dogon statuette (Mazel *et al.*, 2008): (left) distribution of proteins; (centre) distribution of carbohydrates; (right) spatial localization obtained by ToF-SIMS for starch and lipid ions.

resolved technique that can recognize the presence of and distinguish among serpentine polytypes directly in rocks. SR-IR high brilliance allows us to probe tiny areas, as small as 10 μm , as well as a good spectral quality able to distinguish the mineral composition reasonably quickly; finally, it is a non-destructive method. Several thin sections of serpentinitic rocks and prehistoric axes were analysed in reflection mode, and the spectra were acquired directly from specific points of polished stone artefacts. The key results are that all the artefacts analysed are derived from peridotites, ultramafic rocks metamorphosed under greenschist-facies conditions, and characterized by antigorite, diopside and magnetite, sometimes rimmed by penninite. Chemical data demonstrated also a selection of the most suitable raw material for axe production. Mineralogical and petrographic data exclude most Eastern Alps origins, limiting the options to the Hohe Tauern and related secondary deposits of the Drava River hydrographical system. This conclusion agrees with previous studies, as this region is rich in copper ore deposits, which have been exploited since prehistory. These results show the IR microspectroscopy technique to be a helpful tool for the characterization of archaeological lithic material, allowing easy discrimination of the different mineral polytypes, e.g. serpentine present in the stone, without reducing them into powder.

Archaeological bone materials record characteristic markers of life in prehistoric times (dating, climate, environment, diet, human migration). Their isotopic and chemical composition can be combined with palaeontological, archaeo-zoological, anthropological and palaeo-genetic information. However, archaeological bone materials are altered by different post-mortem processes. Although sometimes very challenging, it is key to estimating whether the archaeological information is still reliable, or has been modified during burial. Reiche *et al.* (2010) characterized for the first time the state of preservation of 5,000-year-old archaeological bone sections at the microscale. An archaeological mammal bone fragment ~ 8 cm in size from the Neolithic Chalain Lake site (station 19, 3,000 to 2,970 BC, Jura, France) was selected because of the very good preservation of its organic and inorganic fractions. Bones are nanocomposites composed mostly of two phases: an organic one consisting mainly of type I collagen, and a mineral one consisting of carbonate hydroxyapatite (carb-HAP), closely packed at the nanoscale. Using a method adapted from biomedical research, which avoids bias caused by variation in sample thickness, IR band intensity ratios were used to characterize the state of preservation of the organic and the mineral phases. Specifically the amide I/phosphate ratio ($1,660/1,095\text{ cm}^{-1}$) was used as a measure of the collagen content; carbonate/phosphate ratio ($1,415/1,095\text{ cm}^{-1}$) as a measure of the carbonate content and the ($1,030/1,020\text{ cm}^{-1}$) ratio to evaluate apatite crystallinity. Figure 9 shows the osteon structure of the archaeological bone; the collagen content is homogeneous around the Haversian canal, except in the upper left part, carbonates are clearly enriched in the Haversian canal, and apatite crystallinity is very heterogeneous in HAP. Most of the work done on archaeological bone materials established the state of preservation of the organic and the mineral part separately, without investigating the spatial distribution of the different phases. SR micro-FTIR imaging in transmission mode on archaeological bone thin sections allowed

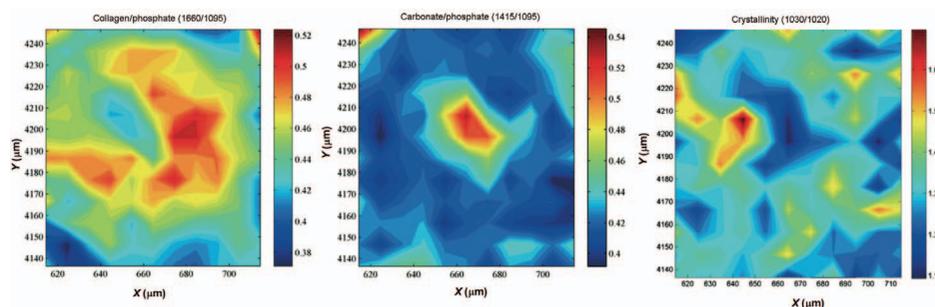


Figure 9. SR-FTIR images showing: (left) the amide I/phosphate ratio ($1660/1095\text{ cm}^{-1}$) corresponding to an osteon area of an archaeological bone sample from the Chalain Lake site (Reiche *et al.*, 2010); (centre) the carbonate/phosphate ratio ($1415/1095\text{ cm}^{-1}$) and (right) the apatite crystallinity (ratio of 1030 to 1020 cm^{-1} bands) for the same osteon. The colour scale goes from red (high intensity) to blue (low intensity) in all images.

investigation of both aspects simultaneously, and provided spatially resolved information on the state of preservation at the microscale. The fine changes in the bone ultrastructure revealed by IR were in agreement with complementary observations of the same specimen. SR micro-FTIR imaging is confirmed to be a powerful tool for obtaining relevant archaeological information and to localize and characterize the less altered zones in the archaeological bone. This information is very useful for the successive selective microsampling necessary for isotopic analysis or dating.

A similar line of research involving IR microspectroscopy concerns fossil bones, their spatial distribution and molecular structure (Lebon *et al.*, 2011). Diagenetic alteration modifying fossil bones over geological time can limit their use as archaeological and palaeontological proxies. The understanding of fossilization processes and the evaluation of the extent of diagenetic alterations of bones remains a major issue in much current research in this field. The complex hierarchical structure of bone tissue and the spatial heterogeneity of the diagenetic alterations, however, induce significant chemical variation at the microscale. To investigate these variations in bone composition at the histological scale, an SR-FTIR microprobe was applied to fossil bone samples of different age and distinct preservation states: bone from Magdalenian layers dated at 15 ka in the Bize-Tournal cave (Aude, France), and samples from the Song Terus site (Java island, Indonesia, 60 ka) were studied. These bones showed partial recrystallization and zones with locally preserved collagen and biogenic carbonates, whereas others showed a recrystallized mineral fraction without any remaining collagen.

Modern bones were used as a reference to determine crystallite size/crystallinity, in addition to the distribution of the collagen matrix and mineral properties. For this purpose, the collagen/phosphate ratio was used to monitor the distribution of the organic matrix. Other specific peak height ratios were used to monitor the composition and structure of the mineral phase, such as the carbonate/phosphate ratio (CO_3/PO_4), the acid phosphate/phosphate ratio (HPO_4/PO_4) content, as well as the mineral

crystallinity after validation and calibration with modern and fossil bones (Fig. 10). Note that a preparation based on PMMA resin impregnation was developed to study heavily altered ancient bones, so that both large and thin sections of fossil bones could be obtained independently of their preservation state and maintaining their histological structure. The distribution of the different components of the mineral matter provided information about the state of preservation of the samples and about the underlying alteration processes. SR-FTIR micro-spectroscopy is indeed an almost unique technique for the identification of preserved and altered areas in bone samples. It may also be used to select samples/parts for palaeo-isotopic reconstructions, or for dating as well as for ancient DNA analysis.

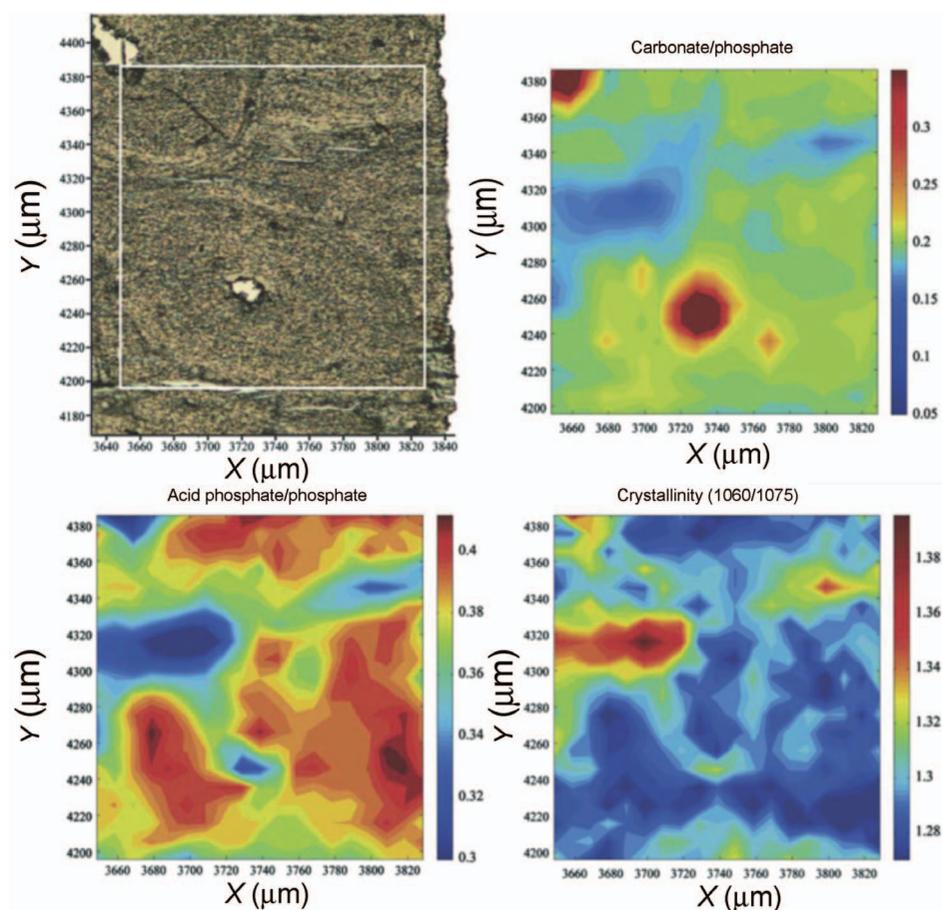


Figure 10. Comparison of (a) the optical view of the analysed area of a bone sample 60 ka old (Lebon *et al.*, 2011) and FTIR colour-coded images showing the spatial distribution of the bone composition; (b) the carbonate/phosphate (CO_3/PO_4) ratio; (c) the acid phosphate/phosphate (HPO_4/PO_4) ratio; and (d) the crystallinity ($1060/1075 \text{ cm}^{-1}$).

Paints consist of different materials/layers: binders, pigments and fillers. Learning about their aging is important for the conservation and restoration of artworks. In an altarpiece painting from the 15th century, traditional egg tempera coexists with the previous drying oil technique. Also, they can exhibit sometimes golden but mostly silvery areas (lustre) obtained by the application of a very thin foil of metal, normally protected from the atmosphere by a varnish or resin, and glued by adhesive substances: egg yolk, drying oil or animal glue. The latter materials often produce reaction compounds which, with time, may result in silver alteration, blackening or even disappearance. In an archetype study (Salvadó *et al.*, 2011), synchrotron-based microFTIR was used to identify organic coatings used to protect silver, the metal foil gluing layers and the reaction compounds in 15th Century Catalunya altarpieces. For example, the Silver degradation area on the altarpiece of ‘Santa Llúcia’ (by B. Martorell 1400?–1452, Museu Nacional d’Art de Catalunya) is shown in Fig. 11. In the same figure, a series of IR spectra obtained from the area in red were obtained from freshly fractured fragments pressed in a diamond cell and in transmission mode *via* a 10 $\mu\text{m} \times 10 \mu\text{m}$ SR-IR microbeam. The various layers are identified easily by their IR fingerprint. The more general result was that the compounds formed were due to atmospheric corrosion and the apparent degree of alteration depends mainly on the state of conservation of the organic protecting coatings. The mechanism of formation of the silver compounds involves Ag chloride and Ag sulfide. The presence of cracks and pores helps the penetration of the atmosphere into the inner layers, and the growth and efflorescence of silver corrosion products induces tensions and flaking of the layers. The sub-millimetric layered structure, the high variability and small amount of compounds present as well as their organic-inorganic nature made the use of micron-sensitive high-resolution technique as SR micro-FTIR essential for this study.

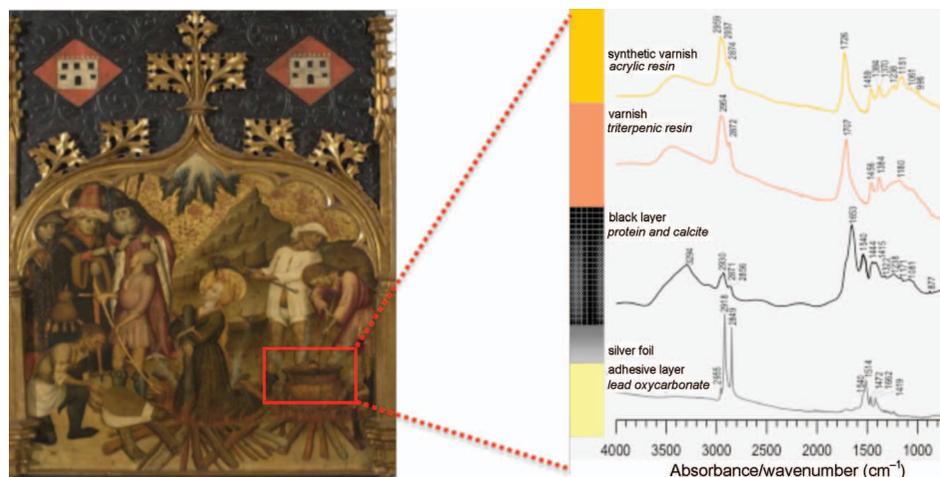


Figure 11. (left) Silver degradation area in red on the altarpiece painting of ‘Santa Llúcia’ (by B. Martorell 1400?–1452, Museu Nacional d’Art de Catalunya, Barcelona). (right) Series of IR spectra showing the various layers of the protected silver area from surface: acrylic varnish (modern restoration), original varnish, black paint over Ag metal foil and adhesive preparation base, respectively.

The high brilliance of SR allows IR spectra to be obtained routinely from the surfaces of reflecting samples, and clearly opens the possibility for non-destructive testing of museum objects with no sampling. The historical contribution (Salvadó *et al.*, 2005) made by SR-FTIR analysis of alteration and corrosion layers in bronze by means of direct IR reflection measurement is interesting. The sample was a 7th Century BC Corinthian-type bronze helmet from The Manchester Museum. This was a fine example of ancient Greek technology, made from a single piece of metal. The art of making such helmets survived until around 1500 AD, but clear information about its manufacture is still lacking. Although FTIR in reflection mode on unpolished surfaces gives poorer results than the ideal transmission mode, the use of SR helps to overcome most issues concerning spectral quality. In this specific example, the detection system had to be adapted to focus on the surface of a large 3D object (Fig. 12). Although only the compounds present on the surface could be determined, the approach allowed selecting different areas of the surface of the object, thus measuring a representative choice of sampling points without extracting fragments from the specimen. One of the outcomes of this study was the determination of the authenticity of the noseguard piece soldered onto the helmet. With FTIR a protein compound associated with animal glue was observed, which was distributed all over the helmet. This glue was very likely applied to prevent further corrosion well before the helmet was acquired by the Museum. Differences were observed between the corrosion products identified: in particular, hydrocerussite on the noseguard piece and malachite all over the rest of the helmet (Fig. 12). This indicates that the noseguard piece was made of a lead-containing copper alloy, whereas the helmet was made of a lead-free copper alloy. Consequently, it is highly probable that the noseguard had been replaced and is not an original element.

In conclusion, SR-IR reflectivity allows the 2D and 3D study of complete objects with a spatial resolution of 10 μm or better, a condition extremely useful for instance in the study of manuscripts (inks, paintings, alterations), and for monitoring the surface degradation and corrosion of large museum objects in a truly non-destructive way.

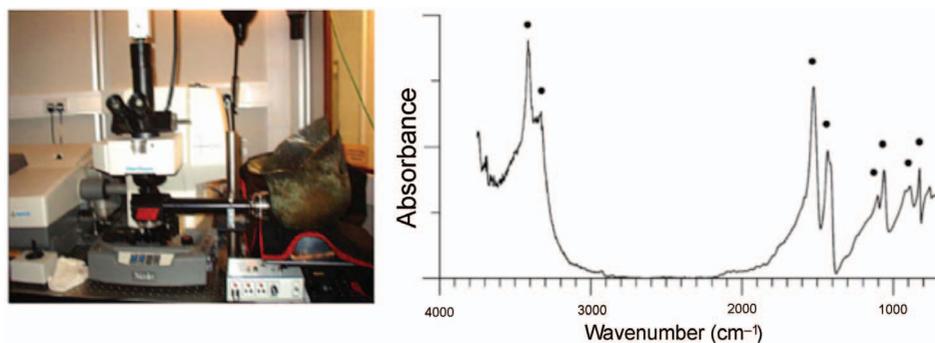


Figure 12. (left) IR microscope coupled to the SR source at SRS Daresbury (UK) and the accessories necessary to collect spectra from an integer bronze helmet in the reflection mode; (right) SR-FTIR spectrum (128 scans, 4 cm^{-1} resolution, spot size 10 $\mu\text{m} \times 10 \mu\text{m}$) collected in reflection mode. The malachite, the CuCO_3 and Cu(OH)_2 bands marked with a dot, allow the alteration of the alloy probed to be monitored.

Ancient paintings are complex materials because of their mixed organic/mineral as well as amorphous/crystallized nature. Restorers and conservators are deeply interested in any useful insight into ancient artistic practices, *e.g.* through the identification of pigments and binders in the matrix. The example chosen concerns Buddhist mural paintings from the Bamiyan site, in the highlands of Afghanistan – middle of Bamiyan valley. Here Buddhism flourished between the 5th and 9th centuries, with the iconic outcome of two Giant Buddhas, magnificent Buddhist paintings in caves, temples, *etc.* Unfortunately famous for its partial demolition by the Taliban, the Bamiyan site was included in 2003 in the World Heritage Danger List, with a UNESCO project developed to decipher the painting techniques and deterioration mechanisms specifically for the Bamiyan Mural Paintings.

In this context, a synchrotron-based IR microprobe was a valuable analytical tool for revealing the two-dimensional molecular and structural compositions of such complex matrices at micrometric resolution (Cotte *et al.*, 2008). Figure 13 shows a painting stratigraphy with average FTIR spectra calculated from the different coloured layers with 1–3 = paint layers, 4 = a ground layer, 5 and 6 = sizing layers applied on the earthen plaster render to provide a better surface for depicting images. Similarities and differences can be observed in spectra 1 to 4, with C–H and C=O ester bands supporting the identification of an oily binder. Hydrocerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$), identified through the characteristic O–H stretching, is concentrated in layer 4. In layer 2, high spots of hydrocerussite are the white visible grains. Cerussite (PbCO_3) – associated mainly with lead white – is concentrated in the white layer 4. In layer 1, copper oxalates and copper hydroxylchlorides are observed *via* the large C=O band of metallic carboxylates. Based on shape and position, a mixture of both copper and lead soaps is then hypothesized. This mixture is present in the two green layers (1 and 2), and the upper layer with copper oxalates could be an alteration of layer 2 due to ageing. In layer 3, the red colour is partially due to goethite (FeOOH), identified by the doublet at $896\text{--}796\text{ cm}^{-1}$, and the large O–H band. Layer 5 contains a mixture of proteins (see amide I band) and polysaccharides (C–O). This suggests the use of mucilage and/or protein-based material, such as hide glue or egg, for the surface preparation. Finally, in layer 6 the specific C=O acid mode is typical of a natural resin (*e.g.* mastic).

In this example, IR spectral quality obtainable by SR was essential to enable distinguishing the various compounds in the stratigraphy. By choosing appropriate regions of interest, it was possible to distinguish ester, acid, amide, carboxylate, carbonate and oxalate groups with the required micron spatial resolution across the specimen.

In the study of the beginning of civilization, the archaeological sites of the first towns in the Neolithic age are rich in information on human life, obtained *e.g.* from house relics. In a recent study, samples from two Neolithic towns were investigated (Anderson *et al.*, 2014): Çatalhöyük in central Turkey with the remains of a town occupied between 7400 and 6000 BC (renowned for elaborate wall paintings in many houses, with designs ranging from patterns/geometric shapes/abstract designs to hunting scenes) and Sheikh-e Abad in the Central Zagros Mountains of Iran which was occupied between 9800 and 7600 BC as a much smaller but earlier site.

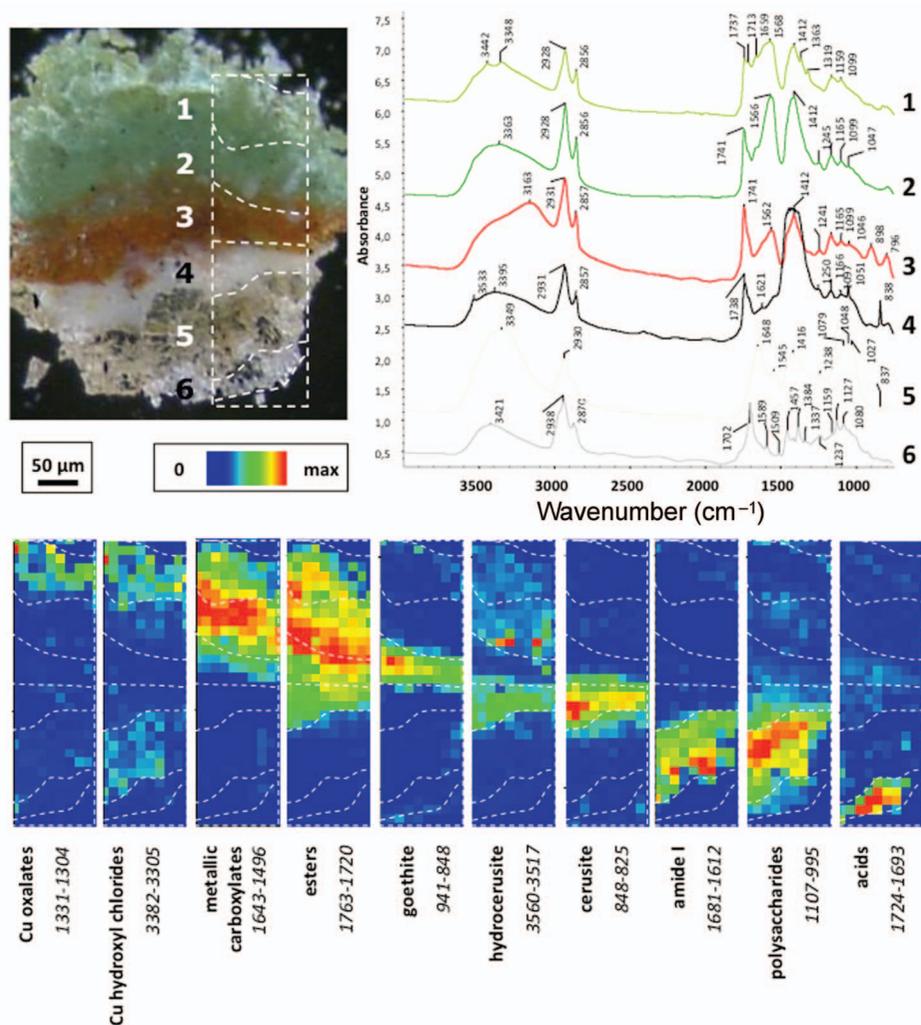


Figure 13. SR-IR stratigraphy of a Buddhist mural painting from Foladi. (Upper, left) Visible light picture; (upper, right) average FTIR spectra; (lower) IR chemical mapping over an area $144 \mu\text{m} \times 384 \mu\text{m}$, step and beam size $12 \mu\text{m} \times 12 \mu\text{m}$.

Interestingly, the internal walls of the mud brick houses in the first had been plastered very frequently by inhabitants. Paintings were applied occasionally to the surface of the plasters, but this artwork would only have been displayed for a short time before being covered over with further layers of plaster. The key sample from Sheikh-e Abad post-dating *ca.* 8000 BC is a roughly shaped ball of red sediment: ~ 5 cm in diameter; it was found in the debris between two pale coloured platform surfaces, which were part of a series of surfaces built in succession and covered with debris like ashes, lithics, burnt bones, shell and reed phytoliths.

Samples containing red pigment have been collected and analysed using a range of techniques, sub-samples were examined also by SR-based IR microscopy (Fig. 14). Thin layers of red paint in a wall painting from Çatalhöyük were found to contain ochre, hematite and clay, as well as an unexpected component: grains of red and colourless obsidian not identified in any previous studies. These small grains of obsidian may have improved the reflective properties of the paint and made the artwork more vivid in the

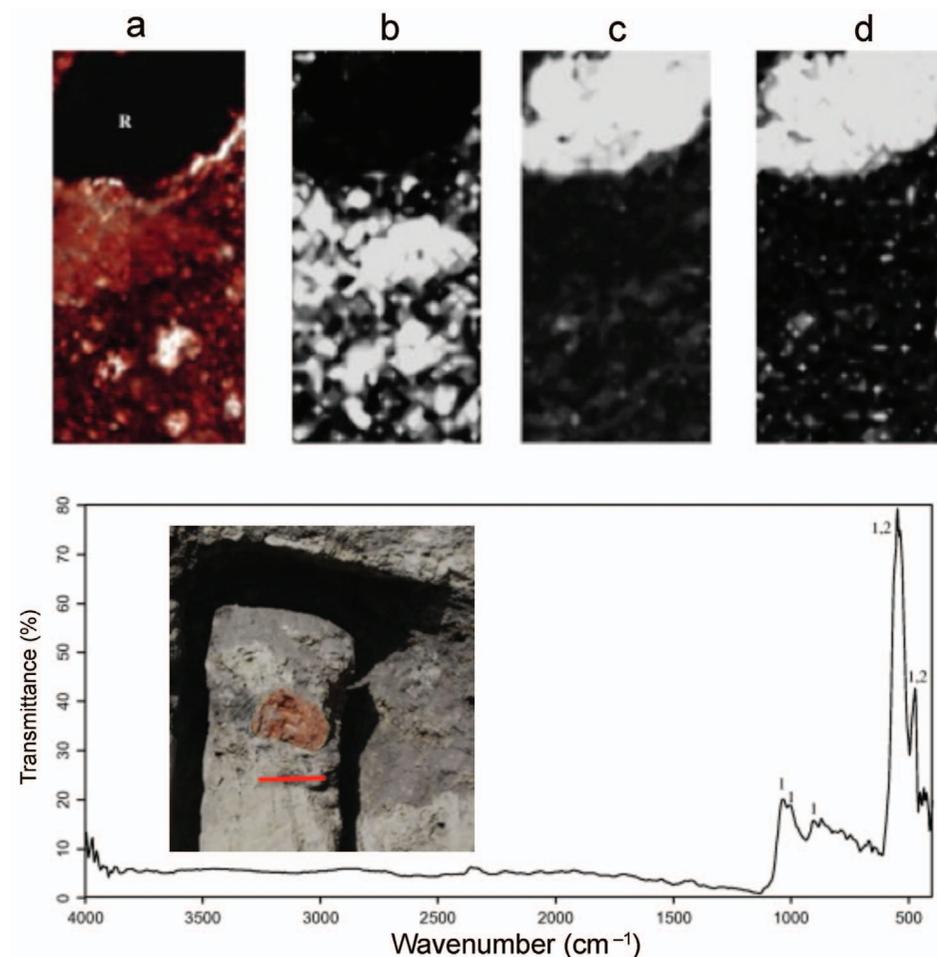


Figure 14. (Upper) SR-IR maps (horizontal size 600 μm) with distribution of minerals across the red sediment from Sheikh-e Abad (inset): (a) visible image of IR mapped area; (b) calcite (CO_3^{2-} asymmetric stretch at 1412 cm^{-1}); (c) kaolin group clay (Si–O–Si and Si–O–Al stretches at 1046 cm^{-1} and Al–O–H bend at 998 cm^{-1}); and (d) clay and hematite (Si–O–Al and Si–O bends and Fe–O lattice vibrations at 547 and 477 cm^{-1}). (Lower) IR spectrum identifying 1 = Clay and 2 = hematite. Inset, locations of block samples at the archaeological site of Tappeh Sheikh-e Abad, Neolithic town in the Central Zagros Mountains of Iran post-dating *ca.* 8000 BC. The red bar $\approx 5\text{ cm}$.

darkness of the buildings. The obsidian was clearly distinguishable by IR microscopy using a synchrotron radiation source, which enabled appropriate spatial resolution. At Sheikh-e Abad the Neolithic people used a red pigment to paint animal skulls and human bones, but no natural source has yet been found in the area. Analysis of the ball of red sediment found on a possible working surface at Sheikh-e Abad revealed that the red colouring is due to the mineral hematite, which was probably obtained from a source of a *terrarossa* sediment in the local area that had not been modified or altered by the Neolithic people. It may have been quite commonly used selectively for specific objects or architectural materials, which is an exciting prospect for new excavations.

Recent papers (*e.g.* Echard *et al.*, 2008; Bertrand *et al.*, 2013) suggest that greater emphasis must be placed on the specificities of ancient materials, and their theoretical implications for the analytical process. These works point out the importance of the *a posteriori* framework of the study of heterogeneous materials considered in their historicity as structuring parameters of a study. Indeed, in many ancient artefacts, the materials under consideration, both of biological or mineral origin *e.g.* pigments, metals, earths, stone, *etc.* show an heterogeneity from the centimetre to the nanometre scale.

Transformation during the lifetime of these materials by various natural processes such as heating, hydration in wet/dry cycles, chemical reactions, or mechanical constraints (*e.g.* hammering) may introduce additional heterogeneities. Ageing and long-term reactivity with the environment may also contribute with non-negligible physical-chemical perturbations.

Examples combining high spatial resolution and spectroscopy had already shown the importance of this approach when looking at the presence of traces of crystalline mineral phases in copper-based green pigments in cross-sections of a painting of the Catalan Gothic painter Jaume Huguet (*ca.* 1415–1492), as markers of the technology used to prepare pigments and of their alteration state (Salvadó *et al.*, 2002). For this specific analysis only the use of a high-brilliance SR source working with a spot size down to a few microns will guarantee a careful investigation of heterogeneities down to the micrometre spatial dimension and mineral compositions of layers of a few micrometres thick.

An example of how spectral and spatial information through SR-FTIR micro-spectroscopy may permit identification of a pigment in the varnish layer of a wooden musical instrument is given in Fig. 15 (Echard *et al.*, 2008; Bertrand *et al.*, 2013). Quantitative information can be extracted by combining the trace chemical composition and the spatial distribution of data. The spatial distribution of data from ancient materials is, in fact, often informative even as a comparative measurement. This is especially true when the spatial resolution and the uncertainty of experimental methods, taking into account matrix and morphological corrections, makes it challenging if not impossible to attain quantitative information.

A typical case study is the observation of the traces of earth-based pigments in the stratigraphy of the varnish of a theorbo (Echard *et al.*, 2008). Figure 15 clarifies why the visualization of the layered build-up in paint cross sections is often more

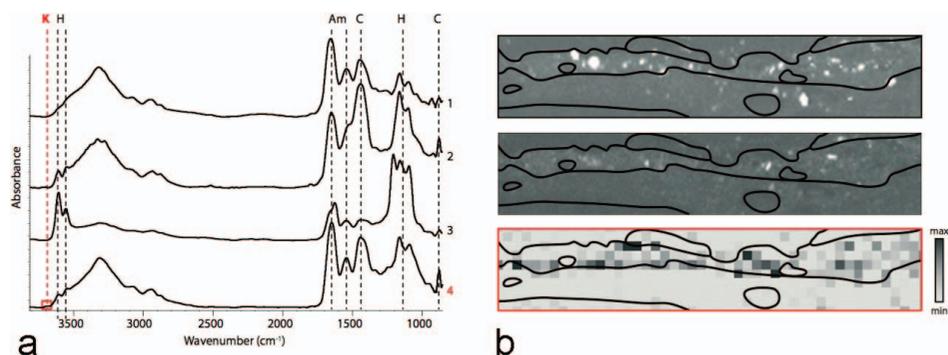


Figure 15. (Left) Comparison among spectra corresponding to a pixel of a first layer (L1) characteristic of a proteinaceous material (1), a grain of calcium carbonate (2), a grain of calcium sulfate hemihydrate (3). The spectrum (4) corresponds to a grain of the earth material located in the layer L2 where the red box is a low-intensity contribution due to the OH-stretching of kaolinite at 3698 cm^{-1} ; (right) comparison of the maps of SR-FTIR signal integrated in the $3715\text{--}3679\text{ cm}^{-1}$ range (upper) and Al (centre) and Si (lower) SEM/EDX elemental maps.

informative regarding the artistic or technological gesture than the accurate local determination of the content in one of binder, pigment, and other components. Indeed, the FTIR spectral signature, although observed with the high brilliance of the SR source, is still weak and only the spatial distribution of this signal over a whole stratum confirms the presence of the compound in the varnish stratigraphy.

Another characteristic example is the identification and localization of varnishes on a musical instrument to reconstruct and understand the violin makers, finishing techniques (Bertrand *et al.*, 2012a). Varnishes from historical wooden instruments are series of layers deposited on the wood surface, each one being a few micrometres thick. Their composition is complex, usually a mixture of organic compounds, occasionally admixed with inorganic compounds, the interactions of which produce strong inhomogeneity from the macro- to the micro-scale. The stratigraphic reconstruction of these layers may provide unique information for conservation scientists, historians and curators. For old instruments written sources are scarce so that information obtained by these studies can be precious not only for recognizing the sources of material, but also for reconstructing differences and similarities among workshops. For these particular studies, sample preparation is a crucial step in accessing high-quality IR spectroscopy data in transmission mode.

Figure 16 shows the comparison of FTIR spectra of the surface stratum and the underlying stratum, both dominated by a very strong and broad carbonyl stretching absorption and by alkyl stretches. The broad band corresponding to the distribution of C=O stretching vibrations is centred at 1.709 cm^{-1} , a value intermediate between that of aged drying oils at higher wavenumbers and that of natural terpenic resins at lower wavenumbers. The discrimination between the two strata can be outlined clearly by mapping the main spectral signatures (Fig. 16 right). The selectivity and sensitivity at the micron-scale of SR-FTIR micro-spectroscopy is demonstrated clearly here, and

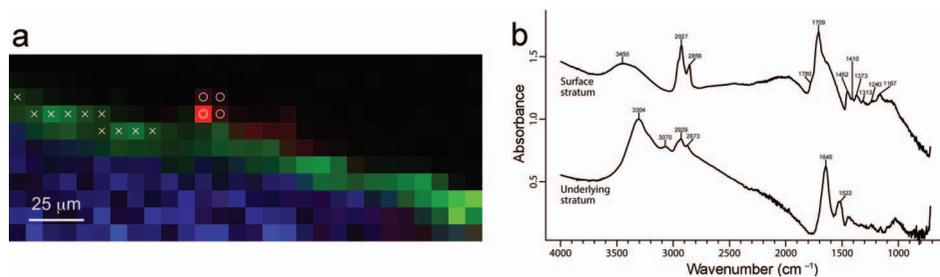


Figure 16. (Left) Mean spectra of SR-FTIR data collected on the underlying stratum (the 10 selected "x" pixels in the map on the right) and on the surface stratum (the 4 selected "o" pixels) of the cello timber; (right) RGB visualization of the FTIR map illustrating the major spectral variations of the stratigraphy where the C–O deformation from cellulose/ hemicellulose is in blue, the amide I band is in green and the C=O stretch from oil/resin compounds is in red.

complementary tests using other techniques did not lead to the identification of additional mineral compounds (driers, pigments) or dyes within the two strata. Although these results have been obtained from a restricted number of artefacts, they allowed the authors to decipher clear differences between major manufacturing techniques used at that time in Europe by famous violin-makers, such as Jacques Boquay and Antonio Stradivari from Cremona. In the studied Stradivari instruments, the underlying stratum was made mainly of a siccative oil (Echard *et al.*, 2010), whereas Boquay used a proteinaceous material on the cello tested.

6. Perspectives for IR and Synchrotron Radiation in conservation and restoration

Notwithstanding the restraints imposed by access to SR facilities, such as typically a six-month call for proposal or beamtime availability at imaging/spectroscopy beamlines, the number of cultural heritage and archaeological studies is growing steadily. At present, most heritage and archaeological studies using SR techniques are limited to materials which can be removed from museums or collections. These include pottery and decorations, glasses, metals, paints and biological remnants, or, very commonly, combinations of organic matter with mineral phases. Typically, the purpose of the investigation is to determine alteration and corrosion dynamics, and/or to understand manufacturing techniques, past-restoration procedures and the provenance of the raw/secondary materials. Due to the difficulty in achieving a statistical validation, in many cases these studies require a comparison with data from similar objects, or samples artificially aged, or contemporary reference materials. This is generally true for microscopy, and more particularly for these challenging specimens an overlooked aspect is the sample preparation (Beltran *et al.*, 2015), which is truly crucial when working on fragile/precious specimens such as mural painting fragments, or brittle bone samples. Many new front-line research proposals have started recently, such as the studies of old documents or ancient books sometimes decorated with precious bezels and gems. For example, the *Evangelarium Marcianum* was the subject

of extensive characterization by various techniques (Sebastiani and Crisostomi, 2012). This fine work of Byzantine jewellery, made in the 13th century and then adapted to be a Missal on the altar of San Marco's Basilica in Venice, is a precious book containing ~100 gems on its front and back binding plates. The majority are coloured glass, polished either in the shape of a fancy cut or a cabochon; others are garnets, almost pure almandine in composition and typical of Czech Moldanubian rocks. Other gems, not well identified, are assumed to be amber. An IR chemical and spectroscopic micro-examination showed this supposed amber to have a silicate composition, probably originally obsidian, which was profoundly altered by the effect of secondary hydration. This volcanic glass is widely distributed throughout the source area, referring to the Mediterranean Sea, but seldom used in gemmology in the rare studies of various forms of its degradation (Mottana *et al.*, 2012).

This is a particularly suitable application of SR-based FTIR microspectroscopy because of its unique specificities: high SNR spectra from its micrometre size spot and imaging capabilities suitable for investigating with a high spatial resolution and in a non-destructive way complex and heterogeneous materials, where small amount of inorganic/organic components are present.

Since the original idea to use synchrotron radiation for historical research studies (Smith, 2003), examinations of cultural and archaeological materials have involved all IR spectral ranges from the near- (NIR), to the far-infrared (FIR) and the THz domains. In the last case, 3D imaging capabilities of small objects can be foreseen in the near future. Development of these measurements is indeed expected to benefit both from the large light flux density and from the long-wavelength IR domain coverage of SR sources.

Studies involving minute scale features or small molecular variations related to local chemical changes are those that may really benefit from the high sensitivity of SR-IR microprobe methods. Anomalies with respect to standard behaviour may occur in mineral phases, crystal defects, *etc.* such as in pigments. Trace minerals can be seen as markers of the technology used to prepare pigments and as the base of their alteration (Salvadó *et al.*, 2002).

In complex mixtures, spectral fingerprinting is essential in order to achieve selective identification. Detection of trace features buried in the intense signal from the matrix will require specific strategies, and, again, the availability of broadband and brilliant SR sources. Conventional laboratory IR microscopy gives useful average spectra over areas of ~50 μm or above. Synchrotron-based micro-FTIR easily allows high spectral quality on most matrices by a micro-spot as small as 5 μm \times 5 μm . Improved spatial resolution may be achieved by the use of objectives incorporating attenuated total reflectance (ATR), because of its high refractive index and consequent higher optical magnification obtainable (see Section 2). The high brilliance of the synchrotron IR source has enormous advantages and allows collection of high-quality spectra from a few μm^2 area of *e.g.* paint cross-section sample in contact with the micro-ATR crystal (Slogget *et al.*, 2010). An intrinsic advantage of the micro-ATR method should be noted, which is the possibility of analysing thick samples in their integral form, or those

specimens not suitable for any thinning method or microtome cutting because of mechanical fragility, *etc.* The counterpart is the contact needed by a 100–250 μm crystal tip with the sample, which may leave a micro-indentation on soft materials.

The combined use of non-destructive structural, spectroscopic and imaging methodologies using SR sources is probably one of the most effective ways of addressing both the spectral quality and spatial resolution requirements typical of cultural heritage and archaeological studies (Cotte *et al.*, 2008; Lluveras-Tenorio *et al.*, 2012). If IR spectroscopy is molecule-specific – thus valuable in providing chemical imaging – X-ray based techniques are relevant for elemental analysis and speciation (Cotte *et al.*, 2010; Bertrand *et al.*, 2012a). X-ray absorption spectroscopy (XAS) experiments can be performed on thin samples, and focusing the beam to sub-micron levels enables 2D selective mapping of many elements. When XAS spectra are acquired in X-ray fluorescence (XRF) mode, the sensitivity is high and can be applied to bulk samples, if not to entire objects. Synchrotron-radiation-based micro-XRF thus allows detection not only of major but also minor or trace elements; in particular, transition metals and rare earth elements which may have major impacts on artefact composition both in the bulk matrix or the decoration. Conversely, XRD can yield information about the atomic order and structure of material (Salvadó *et al.*, 2009, 2013, 2014). For art and archaeology, a key application lies in the use of micro-XRD for the identification and quantification of crystalline phases in a mixed matrix, *e.g.* with reference to diffraction patterns from databases or reference pure standards. The X-ray Absorption Near Edge Spectroscopy and Extended X-ray Absorption Fine Structure (XANES and EXAFS) techniques are highly sensitive and provide precise information on the redox state and local structure of specific elements, respectively. This is particularly significant in artefacts based on amorphous phase materials, such as glasses, ceramics alloys, *etc.* Finally, this chemical sensitivity resulting from SR high brilliance and broadband energy coverage in the X-ray range, provides an unrivalled means of generating elemental maps, especially of higher-Z elements, which is an ideal match to SR micro-IR ability to deliver molecular maps of low-Z-based materials on the same specimens area by a comparably high spatial resolution at the micron scale.

7. Conclusions

Art and archaeological objects are precious, sometimes too large and/or heavy to allow entire objects to be moved to analytical laboratories. Rigorous conditions are applied to their sampling, so that non-invasive and non-damaging studies are a must in research dealing with cultural heritage and historical artefacts. This is the case for jewels as well as for tools, manuscripts and frescos, paintings and statues, *etc.* Most of the time chemical-physical analysis cannot be applied to these specimens, and few spectroscopic methods can be carried out successfully *via* portable instruments. Vibrational microspectroscopy *via* IR offers the possibility of a complete non-destructive analysis with high molecular sensitivity and specificity. The use of SR-IR is of added value because it secures both the highest spectral quality and true micron resolution (Osmond

et al., 2012). Among the complementary technique based on conventional sources, Raman microanalysis must be mentioned for its greater (submicron) spatial resolution. Although with a lower sensitivity, it is a very valuable technique for molecular fingerprinting and mapping, especially of inorganic samples, which are less affected by intense laser beams. On the other hand, organic matrices are more prone to interference issues due to sample auto-fluorescence, sometimes resolved by the use of long wavelength excitation at the cost of a weaker Raman signal.

Vibrational spectroscopy by FTIR *via* compact conventional sources provides valuable molecular specificity, and the use of synchrotron radiation overcomes the spatial limitation when the materials or the objects under analysis are particularly complex or heterogeneous. Spectral imaging of ancient material gives access to topological data that contains additional precious information. Sometimes the ‘spatialization’ of data allows the ‘contextualization’ of the data after recognizing spectral and spatial signatures, *e.g.* with reference to the historical period or geographical provenance. The spatial information of IR spectra can be further processed using a chemometric approach that may identify components or compounds inside the investigated object (Bertrand *et al.*, 2013).

In conclusion, the combination of various micro-analytical and multiple techniques based on X-ray and IR at Synchrotron Radiation facilities is now feasible, and provides a unique asset in such multi-material/multi-disciplinary studies (Salvadó *et al.*, 2010). Having positively passed the exploratory and demonstrative phase described in the previous section, SR micro-FTIR, micro-XRF and micro-XRD can now be considered as mature techniques and recognized methods. They are capable of shedding new light on scientific questions in cultural heritage, conservation and archaeological research that cannot be addressed using conventional laboratory methods. If portable devices support important preliminary characterization, SR brilliance and broadband attractiveness guarantees a full spectrum coverage down to the THz level and a large signal/noise ratio at the highest spatial resolution. Indeed, these unique SR parameters are essential for the compositional analysis of extremely small features on valuable specimens, often heterogeneous and with variable combination of molecular composition, which is a characteristic of most ancient materials (Bertrand *et al.*, 2012b).

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