Show me your yttrium, and I will tell you who you are: implications for fossil imaging
Pierre Gueriau, Clément Jauvion, Cristian Mocuta

To cite this version:
Pierre Gueriau, Clément Jauvion, Cristian Mocuta. Show me your yttrium, and I will tell you who you are: implications for fossil imaging. Palaeontology, Wiley, 2018, 61 (6), pp.981-990. 10.1111/pala.12377. hal-01949420

HAL Id: hal-01949420
https://hal.sorbonne-universite.fr/hal-01949420
Submitted on 10 Dec 2018

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Show me your yttrium, and I will tell you who you are: implications for fossil imaging

by PIERRE GUERIAU\textsuperscript{1,2,*}, CLÉMENT JAUVION\textsuperscript{3,4} and CRISTIAN MOCUTA\textsuperscript{2}

\textsuperscript{1}IPANEMA, CNRS, ministère de la Culture, UVSQ, USR3461, Université Paris–Saclay, F-91192 Gif-sur-Yvette, France; e-mail: pierre.gueriau@synchrotron-soleil.fr

\textsuperscript{2}Synchrotron SOLEIL, L’orme des Merisiers Saint-Aubin, BP48, F-91192 Gif-sur-Yvette Cedex, France; e-mail: mocuta@synchrotron-soleil.fr

\textsuperscript{3}Muséum National d'Histoire Naturelle, Sorbonne Université, UMR CNRS 7590, IRD, Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, IMPMC, F-75005 Paris, France; e-mail: clement.jauvion@mnhn.fr

\textsuperscript{4}Sorbonne Universités, UPMC Univ Paris 06, MNHN, CNRS, Centre de Recherche sur la Paléobiodiversité et les Paléoenvironnements (CR2P UMR 7207), Muséum National d'Histoire Naturelle, 57 rue Cuvier, CP38, F-75005 Paris, France

*Corresponding author
Abstract:

The development of X-ray tomography in the last decade has led to a revolution in palaeontology in providing a means of imaging 3D fossils. In turn, imaging of flat fossils has strongly benefitted from critical improvement of synchrotron X-ray fluorescence (XRF). The latter, which allows mapping the 2D distributions of major-to-trace elements over decimetre-scale objects, usually targets metals with atomic number (Z) up to the strontium (K-shell emission lines); in the same energy domain, L-shell emission lines of heavier elements (particularly lead) can also be analysed. Fluorescence signal from strontium can escape from a depth of few 100 µm in fossils, thereby revealing, due to its substitution for calcium in calcium phosphates (apatite group minerals and bone), hidden fossil bone or phosphatized remains. Nonetheless, strontium similarly substitutes for calcium in calcium carbonates, resulting in the absence of contrast when fossils are preserved in limestone. Here, we show that this issue can easily be overcome by using X-rays slightly higher in energy (17.2 keV and above), to also excite and detect yttrium fluorescence. Together with lanthanides (collectively known as the rare earth elements), yttrium preferentially substitutes for calcium in calcium phosphates, offering anatomical contrasts for a wider range of fossils. This is demonstrated here for three fossils, both vertebrates and invertebrates, from different ages and depositional environments. We further discuss the chemistry behind the different behaviour of strontium and yttrium in calcium phosphates and carbonates. Although yttrium is also found in other (rarer) minerals, its mapping using synchrotron XRF could be used as a proxy to pinpoint calcium phosphates in fossils and other geological materials.

Key words: Yttrium, synchrotron X-ray fluorescence, fossil imaging, apatite.
ADVANCED imaging techniques are now used on a regular basis in palaeontology as they can provide more accurate views of, or reveal new, anatomical characters preserved in fossils that are difficult or impossible to describe using optical photography and microscopy. Actually, since the early microscopic observations of petrified wood by Robert Hooke (1635–1703) in 1665, palaeontologists have often been pioneers in using, and sometimes even developing, new methodologies to extract as much information as possible from their fossils. The last ten years has witnessed the development of a series of X-ray-based imaging techniques that have proved to be fantastic sources of new anatomical information with no, or only limited, sample preparation (see e.g. Sutton et al. 2014; Gueriau et al. 2016 for recent reviews). X-ray tomography, which provides 3D reconstructions of fossils based on local contrasts due to the absorption of X - rays, allows access to the internal morphology of three-dimensionally preserved fossils with an unprecedented level of detail (e.g. Tafforeau et al. 2006). Yet, it suffers from a physical limitation when it comes to the study of flattened fossils, due to the extremely high difference in X-ray absorbance in different directions (along the flat and long dimension of the sample respectively).

Imaging of flat fossils has strongly benefitted from critical improvements in the field of synchrotron rapid scanning X-ray fluorescence (XRF), which produces 2D distributions of major-to-trace elements over decimetre-scale objects, including entire fossil birds (e.g. Bergmann et al. 2010, 2012; Wogelius et al. 2011; Manning et al. 2013; Egerton et al. 2015), with a micrometric lateral resolution or even better. It appears particularly promising as an approach to reveal anatomical details preserved as ‘chemical ghosts’, such as the feather shaft (rachis) in the Thermopolis Archaeopteryx (Bergmann et al. 2010), the pigmentation pattern in the early bird Confusiusornis (Wogelius et al. 2011) or the dentition in a fossil lizard (Edwards et al. 2013), as well as restored areas (Bergmann et al. 2010). Beyond anatomical information, the chemical information provided by synchrotron-based XRF also offers unexpectedly detailed palaeobiological, palaeoenvironmental and taphonomic information through the characterisation of the organic, elemental and mineralogical compositions of fossils (Wogelius et al. 2011; Bergmann et al. 2012; Anné et al. 2014, 2016; Edwards et al. 2014; Barden et al. 2015; Egerton et al. 2015; Gueriau et al. 2016).

The principle of synchrotron-based XRF is very similar to elemental mapping under a scanning electron microscope (SEM-EDX): X-ray photons of the incident beam interact with the inner electrons in some of the sample atoms, creating a vacancy and leaving the atom in an ionised state; the atom returns to its ground state when the vacancy is filled by an outer shell electron, emitting a characteristic XRF photon in the process (Fig. 1D–E). However, instead of electrons, X-ray emission in synchrotron-based XRF is produced by bombarding
atoms with X-rays generated by an X-ray source, here a synchrotron. Synchrotrons are large-scale light source facilities that exist in many countries around the world (www.lightsources.org). A synchrotron possesses several tens of independent experimental end stations, so-called beamlines, which use different energies and/or different setups. A schematic view of a synchrotron, a beamline and a typical XRF setup are shown in Figure 1, together with the XRF principle. The main advantages are that the synchrotron setups can offer an efficient focussing of the X-rays down to sub 100-nm sizes (see e.g. Stangl et al. 2015), can accommodate much larger fossils (Bergmann et al. 2012), and, due to their very large intensity (brightness), are far more sensitive to trace elements. Indeed, the detection limits are in the vicinity of the part per million level (Bergmann et al. 2010; Gueriau et al. 2014, 2015), compared to the ca 0.1–5 wt% level achievable using EDX (Friel and Lyman 2006). Another great advantage of the method is its non-destructiveness and non-invasiveness in most situations.

The important experimental parameter when performing XRF mapping is the excitation energy/wavelength (often expressed as acceleration voltage under a SEM, since the bombarding particles are electrons). The energy limits the range of elements that will be excited, and consequently that can be detected. The very broad and continuous spectral range of the synchrotron radiation up to the hard X-rays offers the ability to finely change the energy of the beam (tunability), allowing the element(s) of interest to be preferentially excited. Synchrotron-based XRF experiments are usually performed using excitation energies in the 3.15–17 keV (kilo electron volts) range, optimised for mapping low-Z elements (Ca and lighter) and high-Z elements (Ca and heavier) depending on the targeted elements. As strontium is known to substitute for calcium in bone apatite, vertebrate palaeontologists use X-rays up to 17 keV X-rays, optimised to excite fluorescence originating from elements up to strontium. Sr maps notably allowed tracking fossil bone physiology (Anné et al. 2014, 2016, 2017 and references therein), as well as to virtually reveal fossil bones hidden under a fine layer of sediment, without the need for any prior delicate preparation (Gueriau et al. 2014). However, the main limitation of the latter approach is that Sr indistinctly substitutes for Ca in calcium phosphates (apatite group minerals; bone) and calcium carbonates, resulting in the absence of Sr contrast in the case of fossils preserved in limestone. Here, we show that this issue can easily be overcome by using X-rays slightly higher in energy (i.e. 17.2 keV and above), to also excite yttrium, which preferentially substitutes for calcium in calcium phosphates.

[Fig. 1 about here]
RESOLVING THE ANATOMY OF FLAT FOSSILS

The reason why synchrotron XRF offers a good alternative to X-ray tomography for resolving the anatomy of flat fossils is that XRF information is not restricted to the very surface of the sample, but can be assimilated from a depth up to several hundred µm. Indeed, X-rays can penetrate the substrate deeply, depending on their energy (the higher the energy, the deeper the penetration) and on the density of the materials (the higher the density, the weaker the penetration). For most fossils (excluding unusual preservation in high-density minerals), X-rays at 16–17 keV penetrate up to a couple of millimetres. Nevertheless, while XRF photons are produced across the whole interaction volume, they have lower energies than the exciting X-rays and can therefore surface and reach the detector only if originating from a shallower depth (photons produced deeper are totally absorbed by the material itself before getting out of the sample; Fig. 2). Still, the detectable information depth depends on two main physical parameters. First, the heavier the element, the more energetic the XRF photons and the deeper they can be detected (note that, consequently, air between the sample and the detector also absorbs XRF photons, so that good low-Z element detection requires vacuum or helium gas environments). Second, several fluorescence emissions can be generated for each element, depending on the electronic orbitals (electron shells) involved in the process; the most energetic arise from the L→K (Kα) and M→K (Kβ) transitions, whereas M→L (Lα) transitions are less intense and ca 7 times less energetic. Consequently, information depth is higher for K-lines than L-lines, and using different fluorescent lines and/or different elements allows tuning of the probed depth and distinguishing surface from volume. Information depth from Sr K-lines in apatite is 200–250 µm. Thus, fossils or anatomic features hidden under a fine layer of sediment can be revealed (Gueriau et al. 2014).

Another important parameter to consider for anatomical reconstructions is the spatial resolution (i.e. the pixel size), which defines the precision and level of details achievable. Synchrotron XRF major-to-trace elemental distributions are collected using mapping (or raster-scanning), i.e. the sequential acquisition of spectra from adjacent regions of the fossil by moving each region (by a lateral quantity of the size of the probe, i.e. the size of the X-ray beam) into the photon beam, line by line. Mapping can be performed following two
modalities. The first mode, primarily implemented at synchrotrons, is known as the step-by-step mode: a XRF spectrum is recorded for each position of the sample, after the sample has moved by the defined scanning step. This implies important dead times – periods of time when no data are recorded – in the acquisition sequence, as the scanning stage has to reach the exact next position to trigger the measurement. Dead times easily reach a few tenth of seconds between each pixel, resulting in scanning times of 1–2 h/cm² at 100 µm resolution (depending on the amount of dead time and the chosen counting time per pixel). The second mode, so-called rapid scanning or flyscan (see Bergmann et al. 2010 and Leclercq et al. 2015, respectively), is at the origin of the increasing use of synchrotron-based XRF mapping in palaeontology, particularly for anatomical reconstruction. It consists of scanning each line by continuously moving the sample: each spectrum (i.e. each pixel) does not arise from a single spot (corresponding to the beam size) but from the sample area scanned during a defined time interval (dwell time). As dead times are suppressed (or at least greatly reduced), this mode allows scanning times of a few min/cm² at 100 µm resolution (up to ~30 s/cm² using a dwell time of ~3 ms and by only recording integrated intensities in 16 spectral regions of interest; Bergmann et al. 2010; Edwards et al. 2013). Such a reduction of the counting time per pixel results in an important loss of signal-to-noise ratio at each pixel, yet the corresponding increase in map speed and map size (or spatial resolution) produces much more XRF spectra that can be summed over a homogeneous area to partly compensate the loss of signal-to-noise. Acquisition times, which depend on the fossil size and the desired spatial (pixel size) and spectral (dwell time) resolutions, are typically of a few to many hours (see Table 1 for indicative examples). Consequently, when high lateral resolution is mandatory to recover fine anatomical details, one has to consider that only a few samples can be mapped over a few days of beam time (typical duration of a synchrotron experiment), and the technique remains restricted to specimens particularly important, rare, exceptional and/or difficult to prepare.

**YTTRIUM MAPPING**

Using 17 keV X-rays (the maximal energy usually used for fossil mapping), it is possible to excite K-lines up to strontium (electron binding energy, 16.1 keV), and L-lines up to palladium (electron binding energy, 16.73 keV). Tuning the energy of the impinging X-rays to 17.2 keV (and above) also allows exciting of yttrium K-lines (electron binding energy,
17 keV) and uranium L-lines (electron binding energy, 17.17 keV). Being slightly higher in energy than Sr photons, the information depth for Y photons is also higher, ca 250–300 μm in apatite, offering even better views of flat fossils (see Gueriau et al. 2014). In addition to the difference in information depth, Y maps have the potential to resolve fossil anatomies in a wider range of fossils, particularly where fossils are preserved in limestone. Indeed, while Sr substitutes for calcium equally well in bone and calcium carbonates, Y and the lanthanides (collectively known as the rare earth elements; REE), preferentially substitute for calcium in calcium phosphates (see also discussion below).

We present here three cases where anatomical, palaeobiological or taphonomical information could only be inferred from Y mapping (Figs 3–5). Data were collected at the DiffAbs beamline of the SOLEIL synchrotron (Gif-sur-Yvette, France) using an excitation energy of 17.2–18 keV. The incoming X-ray beam was collimated by two bendable mirrors, monochromatised using a Si(111) double-crystal monochromator (energy resolution ΔE/E ≈ 10⁻⁴) and focused using Kirkpatrick-Baez (KB) mirrors (Kirkpatrick and Baez 1948) down to a spot size of 9×7 μm² (H×V, full width at half maximum). The fossils were mounted on a xyz scanner stage with μm accuracy, and orientated at 45° to the incident beam and at 45° to the XRF detector, a 4-element silicon drift XRF detector (Vortex ME4, Hitachi High-Technologies Science America, Inc., total active area: 170 mm²) placed in the horizontal plane. The fossil in Fig. 3 was mapped in step-by-step mode, and fossils in Figs 4 & 5 in flyscan mode (Leclercq et al. 2015). Details about other scan parameters and data processing are available in the figure captions.

Looking for ‘Chemical ghosts’ in Palaeospondylus

Palaeospondylus gunni Traquair, 1890 is a mysterious, fish-like fossil vertebrate of highly debated affinities, which has been assigned to various jawless and jawed vertebrate groups, including both larval and adult stages (Moy-Thomas 1940; Thomson et al. 2003; Joss and Johanson 2007; Newman and den Blauuwen 2008; Johanson et al. 2012, 2017, Gardiner 2016, Hirasawa et al. 2016). It is found in the Middle Devonian (~390 Myr) Achanarras fish bed, Achanarras Quarry (Scotland). The fish bed consists of lacustrine laminites of organic, carbonate (dolomite and calcite) and clastic types (Trewin 1986), so that Ca and Sr maps offer no contrast between the fossil (mineralised cartilage, see Johanson et al. 2010) and the sedimentary matrix (Fig. 3). However, the Y map clearly resolves the fossil morphology. Although the latter does not reveal any new anatomical details, it was here critical to precisely localise an unexpected distribution of copper, surrounding the vertebrae and very specifically
located posterior to the paired rostral sensory structures (see Johanson et al. 2017). Such organised distribution very likely represents palaeobiological (in vivo incorporation) or taphonomic (post mortem incorporation) tissue-specific chemistry, possibly representing the ‘chemical ghosts’ of soft-tissues that could provide new arguments for P. gunni taxonomic assignment.

[Fig. 3 about here]

Visualising the anatomy of a new, rare fossil fish from the Cretaceous of Brazil

The Late Cretaceous Bauru continental basin in Brazil has delivered remains of various dinosaurs, crocodiles, turtles and fishes. Among newly discovered fossils, a teleost fish, largely hidden under a fine layer of sediment, appears particularly interesting as it represents one of the very few articulated specimens ever found at this locality. The new fossil preserves the anterior part of the animal (skull and first vertebrae) in a fine- to medium-grained arkosic limestone (Fig. 4). Due to the arkosic content, the Ca and Sr maps here provide a good view of the fossil, yet the ventral part of the skull and the first vertebrae remain partly hidden under what is probably more concentrated carbonate grains. Only the Y map clearly reveals the anatomy of this new taxon, which appears be a ‘primitive’ teleost. A formal description is in preparation.

[Fig. 4 about here]

Highlighting fossil anatomy for point analyses

Besides vertebrates, yttrium mapping can also be applied to many fossil invertebrates, particularly those from exceptional preservation deposits that preserve soft-tissues as apatite group minerals (phosphatisation), and consequently have incorporated yttrium and the other rare earth elements. For instance, it provided a clearer view of the cephalic and thoracic anatomy of a decapod shrimp from the Cretaceous of Morocco (Gueriau et al. 2014).

Anatomical reconstructions are rarely the primary aim of a synchrotron-based XRF experiment. It often serves as a support for further point analyses, aiming at recovering palaeobiological, palaeoenvironmental and taphonomic information from the fossils, e.g.,
through the collection of a high signal-to-noise ratio XRF spectrum for elemental quantifications (Bergmann et al. 2010; Anné et al. 2014, 2016; Gueriau et al. 2015), or through X-ray absorption spectroscopy, an associated technique that provides detailed information about the oxidation state and coordination environment of a target atom (e.g. Wogelius et al. 2011; Edwards et al. 2014). Points of interest can be selected by using a microscope, set at the beamline to indicate the exact position where the beam hit the sample. However, the sample roughness can easily make this useful tool quite imprecise to finely define such points of interest. The best way to circumvent this problem is to first perform XRF mapping, and then move the sample to a pixel of interest, read on the XRF maps. Furthermore, collecting first a XRF map remains necessary when interested in the chemistry of fossils, and/or ‘chemical ghosts’, i.e. anatomical features which are not visible under optical light (such as, e.g., the unexpected Cu distribution in Palaeospondylus gunni, Fig. 3).

We investigated on the preservation modes of a gladius-bearing coleoid (Dorateuthis syriaca Woodward, 1883, specimen MNHN.F.A68134) from the Upper Cretaceous (~85 Myr) marine Lagerstätten of Sahel Alma, Lebanon (Fig. 5). As it is embedded in lithographic limestone, the Ca map and the Sr map only show a topographical contrast (due to sample roughness), but do not resolve the fossil morphology, which is only seen using the Y map as the fossil is partially phosphatised. The apparent pattern of phosphatisation raises questions regarding differential soft-tissue preservation in such localities.

[Fig. 5 about here]

DIFFERENTIAL INCORPORATION OF Sr AND Y

Sr and Y are known to substitute in trace quantities (up to several wt%) for Ca in the crystal structure of Ca-based minerals, their ionic radii being close to that of Ca in these minerals. In minerals from the apatite family [Ca(1)4][Ca(2)6][(PO4)6][OH,F,Cl]2, calcium is present as Ca2+ and occupies two distinct sites - Ca(1) and Ca(2) - in the apatite crystal structure. The coordination number (CN) of Ca(1) is nine, and that of Ca(2) is seven. The coordination number of Ca2+ in carbonates (XCO3) is mostly six (e.g. calcite and dolomite), but is nine in aragonite. Ionic radii for Ca2+, Sr2+ and Y3+ in these coordinations are given in Table 2.

However, and as exemplified by the contrasting distributions observed in our elemental maps (though information depth is comparable), the incorporation behaviours of Sr
and Y differ between calcium phosphates and carbonates. Incorporation of Sr, Y and the other REEs in fossil bone apatites and geological apatites has been extensively investigated. Substitution and adsorption mechanisms (difficult to distinguish from each other) constitute the most important mechanisms for incorporation of these elements into bone during diagenesis (Trueman and Tuross 2002). Relative Sr, Y and REEs amounts in fossils (hundred to thousand ppm concentration or greater for Sr, Y and the light REEs, less for the heavy REEs) reflect simultaneously the connectivity of the environmental water network, local redox, the specific surface area of the bioapatite nanocrystals and physico-chemical conditions and properties of substituted apatite (Kocsis et al. 2010; Trueman et al. 2011; Trueman 2013; Herwartz et al. 2013). In contrast, very few data exist in the literature for REEs incorporation mechanisms in calcium carbonates. Rankama and Sahama (1950) reported that, although Y can replace calcium in calcite, the substitution is extremely slight. Dawson and Hinton (2003) further showed that while Sr is partitioned to only a slightly greater extent into the calcite than apatite, apatite incorporates higher concentrations of REEs than calcite and dolomite. However, Sr and Y concentrations in naturally occurring apatites and calcites point in that same direction: impoverishment of Y in carbonates compared to Sr, whereas their concentrations in apatite minerals is similar (Rakovan and Reeder 1994; Borsato et al. 2007; Morteani et al. 2013).

[Table 2 about here]

SUMMARY AND PERSPECTIVES

We introduce synchrotron X-ray fluorescence mapping of yttrium as a novel means of resolving the anatomy and chemistry of flattened vertebrate and other phosphatised fossils embedded within limestone and carbonate-rich sediments. In the three examples given herein, from different ages and depositional environments, yttrium is the only element that thoroughly reveals the fossil anatomy. Yttrium distributions can then be used to describe anatomical characters previously hidden under a fine layer of sediments due to its information depth of a few hundred microns in fossils (e.g. in the new teleost fish from the Late Cretaceous of Brazil, Fig. 4), to allow precise localisation of unexpected elemental distribution (e.g. in the mysterious Devonian Palaeospondylus gunni, Fig. 3), as well as to serve as a support for further point analyses (e.g. in the gladius-bearing coleoid from the Cretaceous of Lebanon, Fig. 5).
Although we focus here on yttrium mapping, one has to remember that XRF mapping at 17.2 keV and above does not excite only yttrium but actually excites most elements from the periodic table (K-lines up to yttrium, and L-lines up to uranium), so that it also allows assessing the major-to-trace elemental composition of the fossil under investigation. Since the full XRF spectrum is recorded in each pixel of the map, the presence of other trace elements can be detected, and a full spectral decomposition of the spectra (often performed using the PyMCA data-analysis freeware; Solé et al. 2007) allows their distribution to be displayed and their concentration to be estimated. For instance, this could be particularly interesting in the case of the REEs in offering the ability to non-destructively extract REE patterns, ratios and anomalies in fossils, which potentially can provide palaeoecologic and palaeoenvironmental information (see Gueriau et al. 2015 and references therein).

Finally, we discuss the chemistry controlling the different behaviours of strontium and yttrium in calcium phosphates and carbonates, for which little is actually known. Nevertheless, their dichotomous behaviour is clearly shown from our datasets, and at least two highly promising perspectives arise from our results: (1) synchrotron X-ray fluorescence mapping of yttrium could be used as a proxy (in association with complementary laboratory analyses such as petrography and electron microscopy) to pinpoint calcium phosphates in fossils, as well as other geological materials; (2) the high sensitivity (up to the ppm range) offered by the synchrotron beam could enhance the search for traces of early calcium phosphate (vertebrate) skeletons in the fossil record, particularly in the putative basal chordates from the Cambrian.

Acknowledgements. We acknowledge SOLEIL Synchrotron for provision of beamtime, S. Réguer, D. Thiaudière and P. Joly for assistance at the DiffAbs beamline, as well as N. Leclercq, J. Berthaud and teams at the “control data acquisition” and “electronics” groups of SOLEIL for the development of the flyscan platform. G. Clément (MNHN, Paris) provided access to the *Palaeospondylus* specimen, J.-M. Pacaud and S. Charbonnier (MNHN, Paris) to the gladius-bearing coleoid, identified by R. Jattiot (Université de Bourgogne, France). P. M. Brito (UERJ, Brazil) collected and provided the new teleost fish from Bauru, and information about the fossil locality. D. Germain (MNHN, Paris), C. Cupello (UERJ, Brazil) and P. Loubry (MNHN, Paris) took the photographs, respectively of the *Palaeospondylus* specimen, the new teleost fish from Bauru and the gladius-bearing coleoid. The authors also warmly thank S. Thomas, N. Edwards and an anonymous reviewer, whose comments, suggestions and corrections helped to improve the manuscript. This work was developed as part of the
IPANEMA / MNHN agreement on collaborative research. IPANEMA is supported by ANR within the PATRIMEX EquipEx (ANR-11-EQPX-0034) and by Région Île-de-France in the context of the DIM “Matériaux anciens et patrimoniaux”.
REFERENCES


### TABLE. 1
Indicative acquisition times for synchrotron rapid scanning XRF mapping, depending on the size of the area of interest to be mapped, pixel size and dwell time.

<table>
<thead>
<tr>
<th>map size (cm²)</th>
<th>pixel size (µm²)</th>
<th>dwell time (ms)</th>
<th>acquisition time</th>
</tr>
</thead>
<tbody>
<tr>
<td>2×2</td>
<td>25×25</td>
<td>30</td>
<td>5h20'</td>
</tr>
<tr>
<td>2×2</td>
<td>15×15</td>
<td>15</td>
<td>7h24'</td>
</tr>
<tr>
<td>2×2</td>
<td>15×15</td>
<td>10</td>
<td>4h56'</td>
</tr>
<tr>
<td>5×5</td>
<td>100×100</td>
<td>30</td>
<td>2h05'</td>
</tr>
<tr>
<td>5×5</td>
<td>50×50</td>
<td>30</td>
<td>8h20'</td>
</tr>
<tr>
<td>5×5</td>
<td>50×50</td>
<td>15</td>
<td>4h10'</td>
</tr>
<tr>
<td>10×10</td>
<td>100×100</td>
<td>30</td>
<td>8h20'</td>
</tr>
<tr>
<td>10×10</td>
<td>75×75</td>
<td>20</td>
<td>9h53'</td>
</tr>
<tr>
<td>10×10</td>
<td>50×50</td>
<td>10</td>
<td>11h07'</td>
</tr>
<tr>
<td>50×50</td>
<td>200×200</td>
<td>20</td>
<td>34h43'</td>
</tr>
<tr>
<td>50×50</td>
<td>200×200</td>
<td>10</td>
<td>17h22'</td>
</tr>
<tr>
<td>50×50</td>
<td>100×100</td>
<td>3</td>
<td>20h50'</td>
</tr>
</tbody>
</table>

### TABLE. 2
Ionic radii of Ca²⁺, Sr²⁺ and Y³⁺ depending on the coordination number [CN] of the Ca sites in carbonates [VI; IX in aragonite] and apatite group minerals [VII and IX] (from Shannon 1976).

<table>
<thead>
<tr>
<th>Ion</th>
<th>Ionic radius (Å) [CN]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca²⁺</td>
<td>1.00 [VI]</td>
</tr>
<tr>
<td></td>
<td>1.06 [VII]</td>
</tr>
<tr>
<td></td>
<td>1.18 [IX]</td>
</tr>
<tr>
<td>Sr²⁺</td>
<td>1.18 (+18%) [VI]</td>
</tr>
<tr>
<td></td>
<td>1.21 (+14.1%) [VII]</td>
</tr>
<tr>
<td></td>
<td>1.31 (+11%) [IX]</td>
</tr>
<tr>
<td>Y³⁺</td>
<td>0.90 (-10%) [VI]</td>
</tr>
<tr>
<td></td>
<td>0.96 (-9.4%) [VII]</td>
</tr>
<tr>
<td></td>
<td>1.075 (-8.9%) [IX]</td>
</tr>
</tbody>
</table>
FIG. 1. Synchrotron-based X-ray fluorescence. A–C, schematic view of a synchrotron facility and a beamline (A; © SOLEIL), a typical setup at a XRF beamline (B) and the XRF principle (C). D–E, more detailed representation of the photo-excitation process (D) and subsequent allowed XRF transitions (E), with the main emission lines in bold (after Bertrand et al. 2012). [planned for full page width]
FIG. 2. Schematic view of the interaction volume and probed depth in X-ray fluorescence. A, XRF photons are produced in the whole interaction volume (up to a couple of millimetres in fossils excited by 18 keV X-rays), but higher energy photons (here, Y Kα) can escape from deeper volumes than lower energy photons (e.g., Ca Kα). B-D, in the case of a fossil fish partly hidden under a fine layer of sediment (B), while lower energy photons will only resolve bone visible at the surface (C), higher energy photons such as Y Kα photons can reveal buried features (D). Note that hidden parts may appear lower in intensity than surface parts (D), because pixel intensity is integrated over the whole probed volume (i.e. an average content between bone content and the sediment content). Beam size, volumes and distances covered by the photons in air and the sample (represented by arrows in A) are out of scale. [planned for single column width]
FIG. 3. Synchrotron XRF mapping of *Palaeospondylus gunni* (MNHN.F. GBP 92), Middle Devonian of Scotland. Top, from left to right, dry optical photograph of MNHN.F.GBP 92, ethanol photograph of the area mapped, and Ca, Sr, Y and Cu maps. Bottom, mean XRF spectrum for the entire area and main elemental contributions. XRF data were collected on the DiffAbs beamline, SOLEIL, with scan step of 30$\times$30 μm$^2$ (28,231 pixels) and a dwell time (the defined time interval used to collect one XRF spectrum, i.e. one pixel) of 0.5 s. Total map acquisition time was 7h 23min. The elemental distributions were reconstructed from a full spectral decomposition of the data using the PyMCA data-analysis freeware (Solé *et al.* 2007). Scale bars represent 1 mm. [planned for full page width]
FIG. 4. Synchrotron XRF mapping of a new teleost fish from the Late Cretaceous Bauru group, Brazil. Optical photograph (top left) and Ca, Sr and Y distributions. Bottom, mean XRF spectrum and main elemental contributions (DiffAbs beamline, SOLEIL; scan step: 30×30 μm², 648,000 pixels, dwell time: 25 ms; total acquisition time: 5h 39min; elemental distributions reconstructed from integrated intensities in spectral regions of interest, shown as dark band in the mean spectrum). Scale bar represents 5 mm. [planned for two-thirds page width]
FIG. 5. Synchrotron XRF mapping of *Dorateuthis syriaca* Woodward, 1883 (MNHN.F.A68134) from Sahel Alma, Upper Cretaceous (Santonian) of Lebanon. Optical photograph (top left) and Ca, Sr and Y distributions (Scanned in two parts at the DiffAbs beamline, SOLEIL; scan step: 95×95 μm², 587,808 pixels for the right part, 297,252 pixels for the left part, dwell time: 50 ms; total acquisition times: 9h 34min and 5h 13min; elemental distributions reconstructed from integrated intensities in spectral regions of interest, shown as dark band in the mean spectrum). Bottom, mean XRF spectrum and main elemental contributions. Scale bar represents 10 mm. [planned for full page width]