An Effective Polychromatic X-ray Beam for Quantitative Analysis of Fossil Compositions

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Thomas Myron Tolhurst, candidate for the degree of Master of Science in Physics, has presented a thesis titled, *An Effective Polychromatic X-ray Beam for Quantitative Analysis of Fossil Compositions*, in an oral examination held on November 12, 2013. The following committee members have found the thesis acceptable in form and content, and that the candidate demonstrated satisfactory knowledge of the subject material.

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Abstract

A presentation of preliminary results of an ongoing study of fossils deposited in the Frenchman Formation near Eastend, Saskatchewan and the Wapiti Formation in west-central Alberta, Canada, is given in this thesis. Specifically, those of a tyrannosaur and a hadrosaur from the Frenchman and Wapiti Formations, respectively, are studied and compared to others from these formations. The bulk of the analysis is done using Synchrotron X-ray Fluorescence data collected at the Canadian Light Source in Saskatchewan, Canada. Several methods to facilitate both qualitative and quantitative analysis of this data are used and developed. In particular, a method for replacing a polychromatic X-ray spectrum with an effective set of monochromatic beams is explored. Using these methods, the depositional and diagenetic conditions are analyzed. A clear difference can be drawn between the sample locations, offering an explanation for the exceptional preservation of a three dimensional skin fossil in the latter locality.
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List of Abbreviations

CLS  Candian Light Source

LINAC  Linear accelerator

NIST  National Institute of Standards and Technology

SNIP  Sensitive nonlinear iterative peak clipping

SRM  Standard reference material

sXRF  Synchrotron X-ray fluorescence

VESPERS  Very sensitive elemental and structural probe employing radiation from a synchrotron

XRF  X-ray fluorescence
Chapter 1

Introduction

The focus of this thesis has been the analysis of selected hadrosaur and tyrannosaur fossils from the late Cretaceous period. The specimens come from the Frenchman and Wapiti formations in western Canada. In particular, the analysis looks at features discernible through Synchrotron X-ray Fluorescence (sXRF). Chapter 1 discusses general goals, background and previous work done in this area. Chapter 2 looks at some of the relevant theoretical underpinnings of this work. Chapter 3 details the analysis done and methods used. Chapter 4 outlines conclusions drawn from the work presented here, as well as other contributions made to the Integrated Palaeontology Working Group (University of Regina and Royal Saskatchewan Museum), for whom this work was done.

1.1 Palaeontology

Palaeontology is the study of fossils and their depositional settings to learn about organisms and their ecosystems. There are many ways to approach the problem of understanding past organisms and ecosystems through their fossilized remains. The bias of the fossil record towards the hard parts of animals makes fossilized bones a principal source of information. Macroscopic analysis of bones provides information
on life style, and allows classification of many animals. Microscopically, bone histology can deepen the understanding of the life processes of an animal and its relationship with its environment. Morphological analysis alone on this scale provides information on ontogeny, phylogeny, mechanics and environment [1]. A fossil’s chemistry provides still more information. As with all other characteristics of an organism, its chemistry is intimately connected to its environment. However, fossils are marked by many changes after the life of the original organism. Diagenetic alteration weighs heavily in the study of fossils. Stratigraphy, sedimentology and chemistry are, therefore, integral to all palaeontological research.

New analysis tools and techniques are perpetually incorporated into any field of research. Often they are developed or discovered in other fields. In palaeontology, many of these have been concerned with determining chemical composition. Synchrotron radiation provides many means to examine the chemical makeup of an object of interest, and is the latest tool in palaeontology. With the sensitivity and versatility of modern synchrotron facilities comes the opportunity to reveal new information about past ecosystems. Researches at the University of Regina are proceeding with this object in mind. The work is inherently interdisciplinary, and currently involves physicists, geologists, palaeontologists and biologists. With this diverse mixture of backgrounds, there is tremendous potential for the development of new ideas and the unearthing of new information.

1.2 Previous Work

Applications of synchrotron radiation in palaeontology started with the work of Tafforeau [2], constructing 3D images of fossils for morphological study. This initial work did not exploit X-ray fluorescence (XRF) or absorption to study the chemical makeup of the fossils. Bergmann [3] applied both of these techniques, along with
micro-imaging capabilities, to detail the chemistry of an *Archaeopteryx* from the Solnhofen limestone. It was evident from this work that traces of a fossil’s original chemistry could survive diagenetic alteration. Another early work probed for remnant organic material in an exceptionally preserved reptile skin fossil, adding to the list of synchrotron radiation applications [4]. It was demonstrated that remnant fragments of organic material could in fact be preserved in fossils over vast expanses of time.

1.3 Project Goals

The goals of this research are several. Generally, the group is working towards a detailed description of fossils deposited in the Frenchman Formation in Saskatchewan, Canada, and in the Badlands and regions of Grande Praire, Alberta; though there are other localities being studied. A major component of this work is understanding and cataloguing the diagenetic alterations the fossils have undergone. The more this is understood, the more the fossil chemistry can be linked to the palaeo-environment and the more can be learnt about it. To this end, the chemistry of select fossils and their surrounding sediments are being probed with synchrotron radiation, which allows the detection of elements present in only a few parts per million. Both qualitative and quantitative analysis are being pursued. This is an interesting problem to study for the sake of curiosity, but it also helps clarify the evolution of life and deepens our understanding of it.

1.4 Synchrotron Facilities

A concise history of X-ray science and its evolution, including the development of synchrotron facilities, is given in [5]. X-ray light has found diverse use since its discovery by Röntgen in 1895. The theoretical basis for radiation by accelerated charges can be found in Larmor’s classical (non-relativistic) calculation for the total power radiated
by an accelerated charged particle in 1897 [6], followed by Liénard’s relativistic calculation [7] a year later. By 1945, Schwinger [8] had worked out many of the details for the classical (non-quantum) theory of radiation by relativistic accelerated electrons. This included the characteristic bending forward of the double-lobed, non-relativistic dipole radiation pattern.

Following the creation of the first successful betaron, an early electron accelerator, in 1940 by Kerst [9], considerable interest was drawn to the question of radiative energy losses. With the creation of a 70 $MeV$ accelerator to test ideas for accelerating relativistic particles at the General Electric Research Laboratory, came the visual observation of synchrotron radiation in 1947 [10]. In 1961, several years after exploratory measurements at Cornell [11], the National Bureau of Standards (now the National Institute of Standards and Technology (NIST) ) allowed the addition of a tangent section to their 80 $MeV$ synchrotron. This allowed the start of the first experimental program using synchrotron radiation.

1.4.1 First Generation

Initially, synchrotron radiation was accessed parasitically from synchrotrons used for nuclear and particle physics research. The advent of electron storage rings in the 1950’s and 60’s was a significant step forward for synchrotron radiation research. As opposed to the cycle of injection, acceleration and extraction at a synchrotron, the beam is continuously circulated. This allowed higher beam currents, a stable spectrum of radiation and greater beam stability.

1.4.2 Second Generation

The desire for increased flux of radiation for synchrotron radiation research lead to the establishment of dedicated facilities such as the Synchrotron Radiation Source at the Daresbury Laboratory in the UK [5]. Experiments began at this 2 $GeV$ facility in
1981. Increased demand led to the establishment of dedicated facilities around the world. Energies ranged from 700 $MeV$ to 2.5 $GeV$, allowing research with radiation from the UV to X-ray energies.

### 1.4.3 Third Generation

The European Synchrotron Radiation Facility in Grenoble [5] was the first third generation synchrotron. Operating at 6 $GeV$, it came on line in 1994. These are large facilities, optimized for high brightness radiation and the inclusion of many insertion devices, bending magnets and beamlines. Similar facilities are now operating around the world.

### 1.5 The Canadian Light Source

The Canadian Light Source (CLS) is a third generation, 2.9 $GeV$ electron synchrotron facility, located in Saskatoon, Saskatchewan, Canada ([5], [12], [13] and [14]). An electron gun creates and passes bunches of 0.2 $MeV$ electrons into a linear accelerator (LINAC). The LINAC accelerates the electrons to 0.25 $GeV$, and then passes them to a booster ring which accelerates them to 2.9 $GeV$. At this point, the electrons are injected into the storage ring. Once sufficient current (up to 500 $mA$) is built up in the storage ring, injections stop and the electrons are circulated for twelve hours, when it becomes necessary to refill the storage ring due to the gradual decay of the electron beam. The CLS was operating between 150 $mA$ and 250 $mA$ during shifts dedicated to this work.
Chapter 2

Theoretical Considerations

2.1 Diagenesis

A highly analytical discussion of diagenesis can be found in [15] and [16]. The following discussion is of select topics from these works. Diagenesis is alteration, be it physical, chemical or biological, that affects sediments after deposition. This alteration is continuous from the time of deposition, and generally changes with time. It is through its lens that fossils must be studied. The type of diagenetic alteration will depend on the types of materials deposited and on the conditions of deposition.

2.1.1 Microbial Activity

Following the deposition of organic matter in sediments, bacterial decomposition proceeds through several steps. The steps are linked with the depth below the sediment-water interface and with the consequent concentration of dissolved $O_2$. Aerobic decomposition occurs at or above the interface, followed by nitrate reduction (detrification) in the first few centimetres below it. Sulphate reduction occurs over the space of a few meters under the interface, and methane production takes over below that. Also occurring in the sequence is the reduction of iron and manganese oxides.
Newly deposited organic matter (represented as $CH_2O$) is broken down by aerobic organisms through the reaction $CH_2O + O_2 \rightarrow CO_2 + H_2O$. As $O_2$ levels drop below approximately 5 %, denitrification, the reaction $5CH_2O + 4NO_3^- \rightarrow 2N_2 + 4HCO_3^- + CO_2 + 3H_2O$, becomes dominant. With total depletion of $O_2$, anaerobic bacteria become important. They use the oxygen in iron and manganese oxides, as well as sulphate and organic material, for energy. The overall processes are, sequentially:

$$\begin{align*}
CH_2O + 2MnO_2 + 3CO_2 + H_2O & \rightarrow 2Mn^{++} + 4HCO_3^- \\
CH_2O + 4Fe(OH)_3 + 7CO_2 & \rightarrow 4Fe^{++} + 8HCO_3^- + 3H_2O \\
2CH_2O + SO_4 & \rightarrow H_2S + 2HCO_3^-
\end{align*}$$

followed by the pair of reactions

$$\begin{align*}
2CH_2O + 2H_2O & \rightarrow 2CO_2 + 8H \\
8H + CO_2 & \rightarrow CH_4 + 2H_2O
\end{align*}$$

which result in the production of biogenic methane. The order of this sequence is determined by the energy yield of the reactions [15], [16]. The highest yield process is used until its fuel is consumed. The next highest energy yield process is then used, if its fuel is present.

### 2.1.2 Authigenic Minerals

An authigenic mineral is one that forms in sediments after burial, as a result of diagenesis. These precipitates can form in the pore space between grains, known as cementation, or may fill spaces left by the dissolution of other minerals, known as
replacement. The components necessary for the formation of authigenic minerals may have several sources. They could originate in the same sedimentary unit (redistribution), from bacterial processes or be brought from outside the unit. Replaced elements may be subject to redistribution or total removal from the area.

The salinity of the depositional environment is also of interest as it influences the chemical makeup of the interstitial fluid in the sediment. All locations dealt with here represent deposition in non-marine environments. As a result, authigenic production of minerals such as vivianite \((\text{Fe}_3(\text{PO}_4))\), greigite \((\text{Fe}_3\text{S}_4)\), siderite \((\text{FeCO}_3)\), rhodochrosite \((\text{MnCO}_3)\), reddingite \((\text{Mn}_3(\text{PO}_4)_2\text{H}_2\text{O})\) and various \(\text{MnS}\) compounds can be expected [15].

2.2 Synchrotron Radiation

Radiation from charges in circular motion, synchrotron radiation, is covered in depth in [17]. Here, the discussion in [17] is followed and Gaussian units are used. Radiation from accelerated, non-relativistic charged particles is described by the Larmor result for the total instantaneous power radiated. The angular distribution of this radiation has the classic dipole distribution proportional to \(\sin^2 \Theta\), where \(\Theta\) is the angle between the direction of acceleration and the direction of observation \((\mathbf{n})\) with respect to the charged particle direction. The radiation is polarized in the plane containing these vectors.

Once particles become relativistic, the radiation emitted due to acceleration gains several interesting characteristics. The electromagnetic fields from an accelerated relativistic particle can be derived from the Liénard-Wiechert potentials:

\[
\Phi(\mathbf{x}, t) = \left[ \frac{e}{(1 - \beta \cdot \mathbf{n})R} \right]_{ret}, \quad A(\mathbf{x}, t) = \left[ \frac{e\beta}{(1 - \beta \cdot \mathbf{n})R} \right]_{ret} \tag{2.1}
\]

where \(\beta\) is the particle velocity divided by the speed of light, \(c\), and \(R\) is the particle-
observer distance. The subscript \( ret \) indicates that the potentials are to be evaluated at the retarded time \( t = t' - (R/c) \), with \( t' \) representing the particle’s time and \( t \) the time at the observation point. The fields take the form

\[
B = [n \times E]_{ret} \tag{2.2}
\]

\[
E(x, t) = e \left[ \frac{n - \beta}{\gamma^2(1 - \beta \cdot n)^3 R^2} \right]_{ret} + e \left[ \frac{n \times \{(n - \beta) \times \dot{\beta}\}}{(1 - \beta \cdot n)^3 R} \right]_{ret} \tag{2.3}
\]

The two terms in eq. (2.3) can be distinguished by their dependence on the particle’s acceleration. The first term is dependent on the velocity only and is deemed the “velocity field”. The second term is linearly related to the particle’s acceleration and is called the “acceleration field”. These terms also differ in their dependence on \( R \).

The velocity field falls off as \( 1/R^2 \), like a static field, whereas the acceleration field decreases as \( 1/R \), a characteristic of radiation fields.

The denominators of both terms in eq. (2.3) are extremely important. This is evident when looking at the angular distribution of power radiated by a relativistic charged particle, \( P \). From eq. (2.3) it follows that for a brief acceleration and a point of observation far enough from the source such that \( n \) and \( R \) change little, \( P \) is given by

\[
\frac{dP(t')}{d\Omega} = \frac{e^2}{4\pi c} \frac{|n \times \{(n - \beta) \times \dot{\beta}\}|^2}{(1 - \beta \cdot n)^5} \tag{2.4}
\]

where \( t' \) is the particle’s time. Looking at the particular case of \( \dot{\beta} \) perpendicular to \( \beta \), with coordinates such that \( \beta \parallel \hat{z} \), \( \dot{\beta} \parallel \hat{x} \) and \( \theta, \phi \) are the usual azimuthal and polar angles defining the direction of observation; eq. (2.4) becomes

\[
\frac{dP(t')}{d\Omega} = \frac{e^2}{4\pi c^3 (1 - \beta \cos \theta)^3} \left[ \frac{1}{\gamma^2(1 - \beta \cos \theta)^2} \right] \tag{2.5}
\]

In eq. (2.5), the effect of the \( (1 - \beta \cdot n) \) becomes more apparent. As the particle’s
speed approaches $c$, the radiated power distribution tilts forward, resulting in a conical beam of forward focused radiation.

Also of interest is the frequency spectrum radiated by a relativistic charged particle. In general, the power radiated per unit solid angle is

$$\frac{dP(t)}{d\Omega} = |A(t)|^2$$

(2.6)

with

$$A(t) = \left( \frac{c}{4\pi} \right)^{1/2} [R E]_{ret}$$

(2.7)

and $E$ given by eq. (2.3). From the relation

$$\frac{dW}{d\Omega} = \int_0^\infty \frac{d^2I(\omega, n)}{d\omega d\Omega} d\omega$$

(2.8)

and the Fourier transform of $A(t)$

$$A(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^\infty A(t) e^{i\omega t} dt$$

(2.9)

it can be shown that the intensity distribution of the emitted radiation is

$$\frac{d^2I(\omega, n)}{d\omega d\Omega} = \frac{e^2 \omega^2}{4\pi^2 c} \left| \int_{-\infty}^\infty n \times (n \times \beta) e^{i\omega(t-n\cdot r(t')/c)} dt \right|^2$$

(2.10)

where $r(t')$ is the location of the particle with respect to the origin. It is assumed that the observation point is far from the region of acceleration such that $n$ is approximately constant.

Due to the narrowness of the pulse in space and time, it is appropriate to make the assumptions that: $\theta$ is small; and only short times around $t = 0$ need to be considered. Assuming that the particle is located at the origin of coordinates at $t = 0$, it can be shown that the energy radiated per unit frequency interval per unit
solid angle as given by eq. (2.10) is

$$\frac{d^2I(\omega, n)}{d\omega d\Omega} = \frac{e^2}{3\pi^2c} \left(\frac{\omega \rho}{c}\right)^2 \left(\frac{1}{\gamma^2} + \theta^2\right)^2 \left[K^2_{2/3}(\xi) + \frac{\theta^2}{(1/\gamma^2) + \theta^2} K^2_{1/3}(\xi)\right]$$

(2.11)

where

$$\xi = \frac{\omega \rho}{3c} \left(\frac{1}{\gamma^2} + \theta^2\right)^{3/2}$$

(2.12)

\(\rho\) is the particle trajectory’s instantaneous radius of curvature, while the \(K_{2/3}\) and \(K_{1/3}\) terms are modified Bessel functions of the second kind [17]. The general form of these functions can be seen in fig. 2.1. The eq. (2.11) describes \textit{synchrotron radiation}. The first and second terms in the rightmost bracket of eq. (2.11) represent terms for polarization parallel and perpendicular to the orbital plane, respectively. Integration over all angles gives the intensity of radiation with parallel polarization to be several times that with perpendicular polarization; synchrotron radiation is then predominantly polarized in the orbital plane.

From the properties of the modified Bessel functions, it can be seen that negligible radiation is emitted for \(\xi \gg 1\). This will occur for both large angles \(\theta\) with
respect to the orbital plane and large frequencies. This has the effect of confining higher frequencies closer to the orbit plane. It also follows that for very large $\omega$, there is negligible radiation at all angles. This fact motivates the definition of a critical frequency, $\omega_c$, beyond which there is negligible emissions at any angle. This is defined by $\xi = 1/2$, and yields the following result:

$$\omega_c = \frac{3}{2} \left( \frac{E}{mc^2} \right)^3 \frac{c}{\rho}$$

(2.13)

For circular motion, a fundamental frequency $\omega_0 = \frac{c}{\rho}$ can be defined. With that, eq. (2.13) motivates the definition of a harmonic number

$$n_c = \frac{3}{2} \left( \frac{E}{mc^2} \right)^3$$

(2.14)

relating $\omega_c$ and $\omega_0$. $E$ is the energy of the particle. Qualitatively, the following equation applies at $\theta = 0$ and for $\omega \ll \omega_c$:

$$\frac{d^2 I(\omega, n)}{d\omega d\Omega} \propto \left( \frac{\omega \rho}{c} \right)^{2/3}$$

(2.15)

Similarly, for $\omega \gg \omega_c$ one can write:

$$\frac{d^2 I(\omega, n)}{d\omega d\Omega} \propto \frac{\omega}{\omega_c} e^{-\omega/\omega_c}$$

(2.16)

These are the general features and description of synchrotron radiation. For periodic, circular motion, the radiation spectrum is discrete. The radiation consists of multiples of the fundamental frequency $\omega_0$. To move from the description based on the passage of a single particle, as described above, to one in terms of the nth harmonic, eq. (2.11) can be multiplied by the repetition rate $c/2\pi \rho$ and the fundamental frequency $\omega_0 = c/\rho$. The former converts energy to power while the latter
“per frequency” interval to “per harmonic”. This results in the following expression:

\[
\frac{dP_n}{d\Omega} = \frac{1}{2\pi} \left( \frac{c}{\rho} \right)^2 \frac{d^2I}{d\omega d\Omega} \bigg|_{\omega = n\omega_0}
\]  

(2.17)

The above relations describe a very broad distribution of emitted frequencies of light extending from infrared to X-ray. This broad distribution is part of what makes synchrotron facilities such diverse research centres. Integration of eq. (2.11) over all angles results in the intensity distribution as a function of frequency. The greatest intensity is emitted at frequencies slightly less than \(\omega_c\) and drops steadily toward higher and lower frequencies. Eventually the limiting cases in eq. (2.15) and eq. (2.16) are reached. For the higher energies routinely achieved at synchrotron facilities, specialized insertion devices are needed.

There are a variety of insertion devices that are present at synchrotron facilities [14]. There are the bending magnets that keep the electrons in their orbits, but also specialized devices for inducing radiation with particular properties. These are known as undulators and wigglers. Equation (2.11) describes well what would be expected for radiation produced by bending magnets. Undulators and wigglers employ a series of alternating magnetic fields to cause a periodic wobbling of the particle. This causes the particle to radiate. The resulting spectrum depends of the amplitude of the oscillation. Such insertion devices can increase the frequency and intensity of emitted photons.

2.3 Photo Absorption and X-Ray Fluorescence

2.3.1 Photo Absorption

The photoelectric effect is of great importance in X-ray Fluorescence analyses. It is the absorption of incident photons (energy \(\hbar\omega\)) by electrons (mass \(m\)) in an atom (\(Z\)
protons), resulting in the ejection of electrons from the atom (into the continuum of states). For a photoelectron effect to happen, the incident photon should carry enough energy to free the electron from the atom (promote the electron to the continuum of states). This differentiates the photoelectric effect from optical absorption, where since electrons remain bound to their atoms, the absorption must be quantized. The excellent quantum mechanical account of absorption phenomena given in [19] will be followed here.

The ejected electrons will have kinetic energies, $T$, given by Einstein’s equation $T = \hbar \omega - I$, where $I$ is the ionization energy for the electron. Since free electrons are unable to absorb photons, interaction probabilities will increase with increase in electron binding energy. In this case, the innermost orbitals will dominate the photo-absorption processes. Several properties of photo-absorption are well demonstrated by considering the effects of the $n = 1$ orbits (K-shell) only.

Using the Born approximation that the incident and final state particles are plane waves, a description for the region where $T \gg I$ can be reached. To avoid the need for relativistic corrections, a further restriction that $\hbar \omega \ll mc^2$ is made. Under these assumptions, the differential cross section for the photoabsorption of a photon (energy-momentum four-vector $k$, polarization $\epsilon$) by an electron ($p$) is

$$\frac{d\sigma}{d\Omega} = r_0^2 \frac{Z^5}{137^4} \left( \frac{mc^2}{k} \right)^{7/2} \frac{4\sqrt{2} \sin^2 \theta \cos^2 \phi}{(1 - \beta \cos \theta)^4}$$

where $\theta$ is the angle between the directions of propagation of the incident photon and final state electron; $\phi$ is the angle between the $(pk)$-plane and the $(ke)$-plane; $r_0$ is the classical electron radius.

Noteworthy is that the majority of photoelectrons are emitted in the direction of $\epsilon$, and that there are no emissions in the forward ($k$) direction. There is a relativistic $(1 - \beta \cos \theta)^4$ term resulting in an increased probability for electron emission toward
the forward ($k$) direction. This is the same relativistic term that appeared above (eq. (2.1) - (2.5)) for the emission of light from relativistic charged particles.

To reach a result for the total cross section for photoelectric absorption in an atom’s K-shell, eq. (2.18) is integrated over all angles, and then multiplied by 2 to account for the number of K-shell electrons. The $\beta \cos \theta$ term can be ignored in the present non-relativistic case, giving:

$$\sigma = \phi_0 \frac{Z^5}{137^4} 4\sqrt{2} \left( \frac{mc^2}{k} \right)^{7/2}$$

(2.19)

where $\phi_0 = \frac{8\pi r_0^2}{3}$ is the Thomson scattering cross-section ([19], [17]).

In the energy neighbourhood of an absorption edge, modifications to eq. (2.19) are necessary. For heavy elements or $T \sim I$, Born’s approximation is not valid and exact wave functions must be used. The result in this case is:

$$\sigma = \frac{128\pi \phi_0}{Z^2} \frac{137^3}{I} \left( \frac{I}{k} \right)^4 \frac{e^{-4\xi \arccot \xi}}{1-e^{-2\pi \xi}}$$

(2.20)

where $\xi = \sqrt{\frac{I}{k-I}}$ is the ratio of the ionization energy to the electron kinetic energy.

Equation (2.20) is the same as eq. (2.19) with a multiplicative factor that reduces $\sigma$ in the neighbourhood of the absorption edge. Considering the initial assumption that $T \gg I$, these relations will not be accurate near the absorption edge. Describing this region, as well as the photoelectric effect for outer orbitals, is complicated by the need to use exact wave functions. As opposed to theoretical values, the tabulated data in [20] are used to describe photoelectric absorption in this research.

2.3.2 Fluorescence

After a photo-absorption event, the atom is left with a vacancy in one of its (inner) orbitals. An electron from an outer orbital will quickly decay to fill it, emitting a
photon of energy $h \omega = E_b - E_a$, where $a$ and $b$ denote the initial and final atomic states. Not all electrons will have the same transition rate, nor be able to transition to the vacancy left by the removed electron. The transition rate will generally decrease with increasing energy difference between the states. Further, quantum selection rules allow only certain transitions to take place. Transitions where $\Delta n \neq 0$, $\Delta l = \pm 1$ (dipole transitions) and $j = 0$, $\pm 1$ are allowed, where $n$, $l$ and $j$ are respectively the principle, azimuthal and inner precession quantum numbers.

The Siegbahn notation [21], [22] is a common nomenclature for fluorescence photons that can be used to relate a photon to a particular transition. The value of the principle quantum number, which specifies the orbital energy, determines the “shell” of the initial state electron. Shells are labelled K ($n = 1$), L ($n = 2$), M ($n = 3$) and so on for higher values of $n$. Transitions to the shell form a “series” of emission lines and are designated by Greek letters with subscripts. The lines are typically labelled $\alpha_1$, $\alpha_2$, $\beta_1$ . . . in order of the relative strengths of the lines in the series. A Greek letter without a subscript is often used for the sum of two or more lines, which is practical when certain lines cannot be resolved. In particular $K\alpha = K\alpha_1 + K\alpha_2$ and $K\beta = K\beta_1 + K\beta_3$ will be of interest.

### 2.4 Scattering

Aside from the photoelectric effect, elastic (coherent) and inelastic (incoherent) photon scattering processes are relevant at the photon energies used here. The possible scattering processes are Thomson Scattering, Rayleigh Scattering ([17], [19], [23]), Raman effect ([19]), and Compton Scattering ([17], [19], [23]). Their respective cross sections vary with the energy of the photon ([5], [19]), with Compton Scattering dominating for higher energies ($k > 10$ keV).

Photon scattering processes are one of the main sources of background in the
X-ray fluorescence spectra. Elastic and inelastic scattering of the incident photon beam off the sample being studied are sources of the background continuum in the spectra. The variation in the total scattering cross section also sets limits on the accuracy of assumptions made in data analyses. Scattering effects in the Silicon detector contribute additional background. The discussions in [19] and [23] are followed here.

2.4.1 Raman Effect

For the non-relativistic interaction between photons and electrons, the Hamiltonian in the Coulomb gauge ($\nabla \cdot A = 0$ and $\Phi = scalar\ potential = 0$) is:

$$\hat{H}_{int} = \frac{e^2}{2m_e c^2} A^2 + \frac{e}{m_e c^2} A \cdot \mathbf{p} = H^{(2)} + H^{(1)}$$  \hspace{1cm} (2.21)

The first and second terms represent double and single photon processes, respectively. Emission and absorption are, to first order, single photon processes. The number of photons between the initial and final state changes by one and so $H^{(2)}$ can be ignored. Scattering is a two photon process and both terms in eq. (2.21) need to be considered. The total number of photons between the initial and final states changes by two. For scattering, this could be the simultaneous absorption and emission of a photon. Two-photon events occurring through $H^{(1)}$ must pass through intermediate states that differ from previous state by only one photon.

The initial ($i$) and final ($f$) states of the scattering between an electron/atom (energy $E$) and photon (energy $k$) are related through conservation of energy such that:

$$k_f - k_i = E_f - E_i$$ \hspace{1cm} (2.22)

If $k_f = k_i$ the scattering is coherent, the photon energy does not change and the atom is left in the same state. This is Thompson/Rayleigh scattering. When $E_f \neq E_i$, the
atom is left in an excited state where $\Delta k = \Delta E$. This is the Raman effect.

For low photon energies, $E_i$ and $E_f$ are the energies of different atomic states. Summing over all the intermediate states ($n_k$), and assuming $k \neq E_f - E_i$, the differential scattering cross section is:

$$\frac{d\sigma}{d\Omega} = \frac{r_0^2 k_f}{k_i} \frac{1}{m_e c^2} \sum_k \left( \frac{p_{f,n_k} p_{i,n_i}}{E_i - E_k + k_i} + \frac{p_{i,n_i} p_{f,n_k}}{E_i - E_k + k_f} \right) + \delta_{n_f,n_i} \cos^2 \Theta \right)^2 \quad (2.23)$$

where $p_i$ and $p_f$ are momentum components in the direction of polarization of $k_i$ and $k_f$, respectively. For coherent scattering ($k_i = k_f = k$), as the photon energy $(k)$ increases, the summation term decreases in size with respect to the $\cos^2 \Theta$ term, and the cross section for non-relativistic scattering from a free electron (Thompson scattering) is obtained.

As the energy of the incident photon increases further, a new phenomenon occurs. As $k$ becomes greater than the ionization energy, $I$, the electron’s final state may reside in the continuum; the atom will be ionized. In such a case the scattered photon will have energy

$$k_f = k_i + (E_f - E_i) \quad (2.24)$$

where $E_i = I$. This is a species of Raman effect. Since the final state electron is in the continuum of states, this process gives rise to a very broad scattered peak beside the coherent scattering peak. This effect may be observed in XRF spectra. It is manifested in broad peaks, shifted from known emission lines by an energy $\sim I_Y$ for scattering off an electron in state $Y$. Eventually, for very high energy incident photons, the electron participating in the scattering process, though bound to an atom, can be considered as free. This relativistic process is known as Compton scattering.
2.4.2 Compton Scattering

When photon energies are large compared to the binding energy of the electrons in an atom, the Compton scattering cross section can be calculated by the Klein-Nishina formula ([19], [23]). Relativistic energy and momentum conservation for photon scattering at a final angle $\theta$ relative to the incident photon beam direction results in the relation:

$$\hbar(\omega - \omega') = \hbar\omega \frac{\gamma(1 - \cos\theta)}{1 + \gamma(1 - \cos\theta)}$$

between the initial, $\hbar\omega$, and final, $\hbar\omega'$, photon energies, where $\gamma = \frac{\hbar \omega}{m_e c^2}$ ([23]). This process is dominant for high energy photons ($k > 10 \text{ keV}$).

2.4.3 Thomson/Rayleigh Scattering

These are the elastic scattering phenomena between photons and electrons. Negligible energy is transferred to the electron, but the direction of the photon is changed; therefore, this still leads to attenuation of a photon beam. In the low energy limit ($k \ll m_e c^2$), the Compton Scattering cross section reduces to the Thomson scattering cross section. This describes the elastic scatter of a photon from a free electron or nucleus. Rayleigh Scattering is the coherent scattering of a photon from the atom as a whole. All electrons participate in a coherent manner, redirecting the photon without changing its energy [23].

2.5 Detecting X-rays

There are a variety of means for detecting X-rays and other forms of ionizing radiation. They all depend on the deposition of energy into the medium through which the radiation is passing. For charged particles, energy loss to the medium is continuous.
As a result, the mean energy of the radiation decreases as it passes deeper into the material. Neutral particles, including photons, suffer no such depletion. The energy of the photon is unchanged until its removal from the beam through absorption or scattering. It is the charged particles freed, if any, in the interaction of the photon with the detection medium that are detected. Elastic scattering removes photons from the beam without loss of energy, but they may still interact with the medium in the same way as the unscattered photons. Although removed from the beam they are still likely to interact resulting in the release of charged particles. The subjects of particle detection and detector characteristics are covered well in [23]. The relevant results are summarized below.

2.5.1 Ionization Chambers

The characteristics of a gas filled radiation detector are dependant on operating conditions such as voltage and detector geometry. All such detectors rely on collecting the ionization products of ionizing radiation that passes through the detection volume. The first necessary occurrence is that the gas in the chamber is ionized, as opposed to merely excited, giving rise to ion-electron pairs. For photons in the keV energy range, ionization is the principle interaction. What happens to the electrons freed in the primary excitations is dependant on the chamber voltage, and distinguishes the different detector types in this category.

If the chamber voltage is too low, the ion-electron pairs will simply recombine under their mutual electromagnetic attraction. Increasing the voltage sufficiently, but not so much that the freed electrons can ionize the gas, stops recombination and all of the ion-electron pairs will be collected. This is the condition that defines an ionization chamber. The current read from the chamber will be indicative of the number of photons passing through it. Should the voltage be increased to a point where the free electrons can ionize the gas, the chamber becomes a proportional counter. With an
appropriate choice of geometry, a chamber operated in this voltage region will produce a signal that is proportional to the energy of the ionizing radiation passing through the detection volume. Further increases in voltage reduce the proportionality between current and energy until all proportionality is lost in the Geiger-Müller region. Here, the detector output is the same regardless of the energy of the ionizing particle and is used for counting purposes.

There are several ionization chambers present on the VESPERS beamline at the CLS. The output of the “IPREKB” chamber is of most relevance. This is a $N_2$ ionization chamber situated just upstream of the irradiated sample. The voltage on the chamber is maintained such that the current is always proportional to the incident beam intensity. In all data sets, the output of IPREKB is recorded with each datum. The data are then normalized to the incident beam intensity to allow the comparison between different data sets.

2.5.2 Si Detectors

Detectors made of crystalline semiconductor materials, such as Si and Ge, share many aspects of their basic functioning with ionization detectors, but there are some key differences. Of great interest is the increased energy resolution that they offer.

The defining feature of a semiconductor is that its outer atomic shells exhibit an energy band structure (fig. 2.2), which arises from the periodic arrangement of atoms in the crystal and a resulting overlap of electronic wavefunctions. The bands are designated valence, forbidden (an energy gap with no allowed states) and conduction. Electrons in the valence band are localized to particular atoms in the lattice, whereas those in the conduction band are not. The size of the energy gap is what differentiates semiconductors, conductors and insulators. Conductors have no energy gap, leaving electrons free to move about the lattice. Insulators have a large energy gap ($\sim 6 \text{ eV}$), making it improbable for electrons to move from the valence to
the conduction band. In semiconductors, there is a modest gap on the order of an $eV$. Such a gap can be appreciably overcome due to thermal energies or energy added by radiation. This energy gives the order of magnitude of the energy resolution possible with semiconductors; an order of magnitude better than ionization detectors.

Figure 2.2: Figure from [25]. (a): Energy band structure. Insulators, semiconductors and conductors are distinguished by the magnitude of the energy gap. The gap is $\sim 6\, eV$ in insulators, $\sim 1\, eV$ in semiconductors and nonexistent in conductors. Electron-hole pairs can be created by promotion of valence band electrons to the conduction band. (b): The basic design of a silicon drift detector. $p^+$ electrodes create a parabolic potential, which pushes the $e^-$ to the centre of the Si wafer. The $e^-$ are subsequently collected by the $n^+$ anode.

Another interesting feature is the charge carriers in a semiconductor device. In analogy to ionization, there are positive and negative carriers: holes and electrons, respectively. The holes are not particles, but the vacancies left in the valence band by electrons excited into the conduction band. Nonetheless, they behave as positive particles and contribute to the current in the detector.

Electrons excited to the conduction band will eventually recombine with holes at a later time. This lifetime is of importance for charge collection. If the mean time for recombination is close to or less than the time for charge collection, a significant reduction in resolution will result. Impurities in the lattice will tend to reduce the lifetime of the excited electrons by creating recombination centres or encouraging
trapping. In both cases, energy levels are created in the forbidden zone that can enhance recombination, or simply hold the electrons outside of the conduction band. In the absence of impurities, electron and hole lifetimes should be as long as a second; an effect of energy and momentum conservation. Actual lifetimes are on the order of nanoseconds, underscoring that perfectly pure crystals are not realizable.

One way of overcoming impurities is doping the semiconductor, which involves adding atoms with one more or less electron than the original atoms in the lattice. These are known as doped or extrinsic semiconductors. Semiconductors doped with pentavalent atoms are known as n-type. Those doped with tetravalent atoms are called p-type. In the case of heavy doping, a superscript + is added. Doping creates donor and acceptor states in the forbidden zone. Such states differ from other impurities in their closeness to the conduction (donor) and valence (acceptor) bands. The former creates an excess of electrons in the conduction band while the latter an excess of holes in the valence band. The overall effect is to overwhelm the effects of impurities in the semiconductor. With an improved ability to grow ultra pure crystals, has come the use of intrinsic semiconductor detectors. Low impurity levels means that there are sufficient charge carriers in the lattice for the detectors to function efficiently.

Another phenomenon of interest is the formation a depletion zone under application of a potential across a semiconductor. The depletion zone is a region free of charge carriers that forms due to the migration of electrons and holes in the potential. This creates a situation analogous to the neutral atoms/molecules in an ion chamber. Once energy is imparted to electrons in the depletion zone creating electron - hole pairs, they are swept away by the potential to form an electronic pulse. The size of the depletion region is dependant on the voltage and can consume the entire volume of the semiconductor.

For silicon it typically requires $\sim 3.6 \, eV$ to create an electron - hole pair (a
few $eV$ go into exciting lattice vibrations). This results in energy resolutions an order of magnitude higher than in ionization-based detectors, where tens of $eV$ are needed to create charge carrier pairs. The difference is due to the energy resolution’s proportionality to the ratio $w/E$, where $w$ is the mean energy needed to produce a charge carrier pair and $E$ is the energy deposited in the medium. For the same energy transfer to the detection medium, materials with lower $w$ will typically result in higher energy resolution.

There are many configurations used for semiconductor detectors for varying needs. One is the silicon-drift detector. Such detectors are position sensitive, can handle high count rates and require a small volume of electronics when compared to similar strip semiconductor detectors. The basic design of the silicon-drift detector, shown in fig. 2.2, uses $p^+$ electrical contacts placed on either side of a silicon wafer, creating depletion zones that extend partway toward its centre. A $n^+$ electrical contact at one end of the wafer fully depletes it. A parabolic potential is created in the wafer, pushing electrons to the its centre. The electrons then drift allong this region to an electrode at the side of the device where they are collected and form a signal.

The detectors used on the VESPERS beamline are Hitachi High-Technologies Science America Inc.’s Vortex-90EX and Vortex-ME4. Both are high purity Si drift detectors with active areas of 50 $mm^2$ and 170 $mm^2$, respectively. Respective sensitive thicknesses are $350 - 450 \mu m$ and $350 \pm 30 \mu m$. Both detectors are covered with 12.5 $\mu m$ thick beryllium windows [24].

### 2.5.3 Detector Dead Time

The dead time is the time required by a detector, or detector element, to process an event. This will be dependent on several factors, but two categories can be considered, extendable and non-extendable [23]. An extendable dead time results when the detector remains sensitive to other events during the the processing of earlier events.
In this case, if the event rate is sufficiently high the processing times will overlap and pile-up. The result is an extended time where events cannot be accepted. This can even result in “paralysis”, where no events are registered. Non-extendable dead times occur when the device does not accept other events until the previous one has been processed. Often a device will be a combination of these two types.

On the VESPERS beamline, the dead time is corrected for by applying two count rates that are recorded during data collection. The ratio between the total and processed counts gives a multiplicative factor for adjusting the recorded emission spectra. This correction is applied to all data sets, which is necessary due to fluctuations in dead time with sample composition and incident beam intensity.

2.5.4 Escape Peaks

A detector’s efficiency for detecting any given type of radiation is dependant on the type and energy of the radiation, and on the detector material and design. Semiconductors often have a dead layer of material that absorbs radiation, but does not produce a signal. This reduces the detection of lower energy photons in particular, since they are less penetrating than higher energy photons. The detector’s thickness is also important as it influences the probability of radiation passing right through the active portion of the detector. Also related to the geometry is the escape peak phenomenon [25]. In high energy physics the term is used to refer to lower energy peaks due to the loss of the electron or positron in pair production events. At the energies considered here, pair production is not energetically allowed, but escape peaks still occur. In this instance, it simply refers to peaks resulting from incomplete collection of the incident photon energy. This dominates for lower energy photons that are likely to interact in the outer layers of the detector. Ionization events near the detectors edge carry an appreciable probability that the photon(s) released in the de-excitation of the atom will leave the active volume of the detector, undetected,
constituting a loss of energy. This loss will be equal to the energy of the escaped photon(s). Therefore, a shifted peak will appear at an energy equal to the initial photon energy minus that of the escaped photon(s) [25].

2.6 Fundamental Parameters Analysis

There are many methods for determining the concentrations of elements in samples through XRF analysis. Many of these are dependent on fluorescence standards, while others are computation based. The Fundamental Parameters method relies on applying basic principles of interactions between photons and matter, along with tabulated data, to determine concentrations in a sample. The method used here is based on those presented in [22] and [25].

Regardless of the details of the method, the goal is always to find a way to mitigate absorption and enhancement effects. Both of these result from secondary interactions between elements in the sample matrix (here the matrix refers to the whole of the sample, except the analyte of interest) and the incident and emitted photons. Absorption/enhancement cause deviations from the otherwise linear relation between emitted line intensity and element concentration. Absorption denotes a decrease from the linear trend, and enhancement an increase. The magnitude of the effect is related to the various cross sections of the elements in a sample for photons of different energies. If a secondary element is present with a higher or lower cross section for the incident photons, the observed intensity of the element of interest’s emissions will respectively decrease or increase. Similarly, if the secondary element has a higher or lower cross section for the emissions from the atom of interest, than it itself does, the observed intensity will respectively decrease or increase. The combination of these scenarios leads to a net decrease (absorption) or increase (enhancement) in the observed signal from the atom of interest.
2.6.1 Monochromatic Beam

Determining element concentrations using X-ray emission spectra and a fundamental parameters method is based on several probabilities. The probability that the incident beam ionizes a particular atom. The probability of emission of the X-ray emission line of interest from this atom. The probability that the emitted photon arrives at the detector and is detected. These are related to the interaction cross sections and decay rates discussed in sections 2.3 and 2.4. The overarching questions are whether a given atom will absorb a given photon and, if absorption occurs, what is emitted when the atom de-excites?

The relation of the intensity of photons incident on a sample, $I_0$, to the number $I_i$ of a certain spectra line ‘$i$’ observed by the detector, can lead to the computation of the concentration of a certain element in a sample, or, more generically, to the sample composition. These terms are simply related through a series of coefficients, most of which are related to photo-absorption and emission probabilities.

One of the most important terms is the mass absorption coefficient, usually denoted by $\mu$ or $(\mu/\rho)$. Here $\mu$ is used along with a subscript, or subscripts, relating it to a particular atom/material and energy of incident photon. It is a measure of how readily a photon beam is attenuated by some material, whether it consists of one or many different types of atom. It is directly proportional to the the total interaction cross section ‘$\sigma$’, defined such that:

$$\sigma = \frac{\text{rate of interactions}}{\text{incident particle flux}} \quad (2.25)$$

The total cross section for photon interactions with an atom is the sum of the elastic scattering cross section $\sigma_{es}$, the inelastic scattering cross section $\sigma_{is}$, and the photo-absorption cross section $\tau$. This last cross section is the one of interest, because it is photo-absorption that leads to the emission of characteristic X-rays that can
eventually be detected.

For moderate photon energies ($\sim$ keV) and/or heavier atoms, $\tau \gg (\sigma_{is} + \sigma_{es})$. This is especially true in the neighbourhood of an absorption edge. A comparison of interaction cross sections is given in fig. 2.3. Since this work will always be considering photons near absorption edges, the approximation

$$\sigma \approx \tau$$

is justified. It is good to within a few percent at the photon energies ($2 - 30$ keV) relevant at VESPERS [20]. The validity of the assumption is enhanced by how scattering affects the incident photons, and by how the attenuation of the beam is described. Scattering removes a photon from the beam, but the preceding assumption is that all photons are removed by photo-absorption. Scattered photons are still very likely to be absorbed in the samples considered here (thick samples), improving the total-absorption assumption.

![Figure 2.3](image)

Figure 2.3: Figure from [25] comparing mass attenuation coefficients for scattering and photo-absorption in select materials. The mass attenuation coefficients are proportional to the interaction cross sections for the processes, as can be seen from eq. (2.26) and eq. (2.28)

To determine the full form of the mass absorption coefficient, a few parameters
need to be introduced. The interaction probability should be proportional to the density of atoms in the sample:

\[
N_A \rho / M_{\text{atomic}} = \text{number density of atoms} = \tilde{N}
\]

measured in \textit{atoms/cm}^3, where \( N_A \), \( \rho \), and \( M_{\text{atomic}} \) are Avogadro’s number, the material’s density and molar mass, respectively. Multiplying \( \sigma \) by the preceding term gives the probability of interaction per unit length. This is usually called the linear absorption coefficient and is denoted by:

\[
\bar{\mu} = \sigma \tilde{N}
\]  

(2.26)

Multiplying this by the photon’s path length gives the interaction probability.

The intensity of a photon beam as a function of path length \( l \) is then given by:

\[
I(l) = I_0 e^{-\bar{\mu}l}
\]  

(2.27)

It is often desirable to use the mass absorption coefficient in place of the linear absorption coefficient since it is not a function of the sample density. They are simply related such that:

\[
\mu = \bar{\mu} / \rho
\]  

(2.28)

The argument of the exponential in (2.27) then becomes \(-\mu \hat{m}\), where \( \hat{m} = x \rho \).

The key point is that it can eventually be removed from the equations relating \( I_i \) and \( I_0 \) for a thick sample. Thick implies all incident photons are absorbed. This is unlikely to happen, but is a good approximation here, where the majority of samples are \( \sim 0.5 \text{ cm} \) thick.

The next concern is the probability of emission of a given photon after photo-absorption. When an electron in an outer orbital moves to an inner one, the prob-
ability that this transition leads to the emission of a certain characteristic photon is broken up into several constituent probabilities. Their product will give the probability, \( P_i \), that the \( i \)th characteristic photon is emitted.

The first item to consider is that there are two competing effects through which an outer-shell electron is able to decay to a vacancy in an inner orbital. These are photo-emission and the Auger effect. It is the characteristic photo-emissions that are detected in measurements presented here. The Auger effect results in the emission of an electron, which is not detected in this case, though Auger electrons are characteristic of the emitting atom and can be used for spectroscopy. Since an atom must decay through one of these two effects, their respective probabilities are related by

\[
1 = \omega + \kappa
\]

where \( \omega \) is the probability of photo-emission and \( \kappa \) is the probability of Auger electron emission. These probabilities are functions of the atomic number. Auger emission dominates for lighter elements, while photo-emission becomes more prominent as the atomic number increases, as depicted in fig. 2.4.

Which characteristic line is observed depends on which electron was ejected from the atom in the photo-absorption process. This determines where the vacancy is in the atom, as well as which electrons may fill the vacancy as described above. The probability that a vacancy is created in an orbital that can lead to emission of a line \( i \) is denoted \( R_i \). The product \( R_i \sigma \) is the cross section for a particular shell of atom \( i \) (\( i \) is being used for both the atom of interest and the terms associated to the emission line of interest for brevity). \( R_i \) is related to the simple ratio of the photo-absorption probability for photons with energies directly below and above the minimum energy required to remove an electron from the shell \( i \). This ratio is called the edge jump.
ratio, often denoted by $r_i$, such that

$$R_i = 1 - \frac{1}{r_i}$$

A similar term as that described above is used to account for which electron fills the inner shell vacancy, giving rise to the photon of interest in the process. It is a ratio of decay probabilities for particular electrons. As an example, the desired probability $g_i$, for the $K\alpha$ line, can be given by:

$$g_{K\alpha} = \frac{\sum I_{K\alpha 1} + \sum I_{K\alpha 2}}{\sum I_K} \quad (2.29)$$

This equation is a sum of the number of decays that lead to the line of interest, divided by the total number of decays in that series. For a hole created in an atom due to photo-ionization, the probability of emission of a spectral line $i$ is given by the

Figure 2.4: Variation in fluorescence yield for K and L shells with atomic number [5].
product:

$$\omega_i R_i g_i$$  \hspace{1cm} (2.30)

With eq. (2.30), it is largely a matter of composition to reach the desired relationship between \(I_0\) and \(I_i\).

The change in the number of photons in the beam, when it passes through an infinitesimal slice of the material, will equal the number of photons absorbed by that slice (under the assumption \(\sigma \approx \tau\)). This is given by the spatial derivative of (2.27):

$$\frac{dI}{dl} = I_0(-\mu \rho) e^{-\mu \rho l}$$  \hspace{1cm} (2.31)

where \(dl\) is an infinitesimal path length.

Rearranging (2.31) such that only \(dI\) remains on the left hand side of the equation gives:

$$dI = I_0(-\mu \rho) e^{-\mu \rho l} dl$$  \hspace{1cm} (2.32)

This describes the number of photons lost from the beam in an infinitesimal slice of the sample between \(l\) and \(l + dl\). The number of photons absorbed by the atoms is given by (2.32) with the sign reversed. Integrating this over the sample thickness gives the total number of photons absorbed in the sample.

The number of photo-absorptions by the atoms of interest in each thin slice of the sample is known by eq. (2.32). Multiplying this number by (2.30) gives the number of characteristic photons emitted by each slice:

$$dI_{i,em,dl} = I_0 \omega_i R_i g_i (\mu_{i,E_0} \rho C_i) e^{-\mu \rho l} dl$$  \hspace{1cm} (2.33)

The subscripts of the mass absorption coefficient are such that for photons of energy \(E_0\), incident on an atom \(i\), the corresponding coefficient is denoted \(\mu_{i,E_0}\).

In going from a discussion of the sample as a whole (denoted by \(M\)) with density
ρ to the discussion of the element of interest, it is used that:

\[
\mu_{M,E_0} = \sum_{j}^{\text{total\#elements}} \mu_{j,E_0} C_j
\]  

(2.34)

where element ‘j’ has concentration (weight fraction) \(C_j\) in a matrix with \(C_{\text{Matrix}} = 1\). This yields the following equation:

\[
dI_{\text{total,em,dl}} = \sum_{j}^{\text{total\#elements}} dI_{j,em,dl}
\]  

(2.35)

The subscripts \(M, E_0\) and \(i\) will continue to be added to the absorption coefficients to emphasize that they are the coefficients describing the attenuation of the incident beam of photons carrying energy \(E_0\) by the matrix \(M\) or element \(i\). Integrating eq. (2.33) over the thickness of the sample gives the total number of characteristic photons emitted.

The experimental geometry is defined as shown in fig. 2.5. To reach the layer \(dx\), the incident beam must travel through a sample thickness of \(\frac{x}{\sin\phi}\). The amount of the initial beam that makes it to the layer \(dx\) is

\[
I_{\text{reaching} - dx} = I_0 e^{-\mu_{M,E_0} \frac{dx}{\sin\phi}}
\]  

(2.36)
Replacing the $I_0e^{-\mu pt}$ and $dl$ terms in (2.33) by (2.36) and $\frac{dx}{\sin\phi}$, respectively, gives the number of photons emitted by the layer $dx$ when the attenuation of the matrix is taken into account. This form is shown in (2.37).

$$dI_{i,em,dx} = I_{\text{reaching} - dx\omega_i R_i g_i(\mu_i, E_0 \rho C_i)} \frac{dx}{\sin\phi} = \omega_i R_i g_i(\mu_i, E_0 \rho C_i) I_0 e^{-\frac{\mu_{M,i}\rho x}{\sin\phi}} \frac{dx}{\sin\phi}$$

(2.37)

However, two more steps are needed to reach the final result for primary excitations by a monochromatic beam.

The first step is to consider a term that accounts for the matrix’s attenuation of the emitted characteristic photons. Looking at fig. 2.5, it is seen that to account for the matrix attenuation one must multiply (2.37) by an equation similar to (2.33). This results in the following equation:

$$dI_{i,\text{reaching} - \text{detector}} = dI_{i,em,dx} e^{-\frac{\mu_{M,i}\rho x}{\sin\phi}}$$

(2.38)

The second step is to account for the detector solid angle, $\frac{\Delta\Omega}{4\pi}$. This will be the ratio of the active area of the detector that faces the sample to the surface area of a sphere with radius equal to the separation between the point of emission of the characteristic photon and the detector. In the actual concentration calculations, the sample-detector separation is used in order to simplify the mathematics involved. The equation relating the the infinitesimal number of characteristic photons reaching the detector to the excitation of atoms in the layer $dx$ is then given by:

$$dI_{i,\text{reaching} - \text{detector}} = I_0 \omega_i R_i g_i(\mu_i, E_0 \rho C_i) \frac{\Delta\Omega}{4\pi} e^{-\left[\frac{\mu_{M,i}\rho x}{\sin\phi} + \frac{\mu_{M,E_0}\rho x}{\sin\phi}\right]} \frac{dx}{\sin\phi}$$

(2.39)

Integrating the above equation from $x = 0$ to $x = \infty$ gives the end result for emissions from the entire sample. This is the same as to say that the sample is
thick enough such that no photons from the incident beam traverse it, which is a good approximation based on tabulated data in [20]. For example, a 0.5 cm slice of apatite and photons with energies in the $2 - 18$ keV range, less than 0.0001 % of incident photons make it through the sample [20]. Those that make it through, at this percentage, are at the high-energy end of the spectrum. For photons with energies under 9 keV, less than $1 \times 10^{-42}$ % are transmitted [20]. After the integration one has:

$$I_{i, \text{reaching detector}} = I_0 \omega_i R_i g_i C_i (\mu_{i,E_0}) \frac{\Delta \Omega}{4\pi \sin \phi} \left( \frac{\mu_{M,i}}{\sin \psi} + \frac{\mu_{M,E_0}}{\sin \phi} \right)^{-1}$$ (2.40)

This is the final result relating the number of detected photons to the fraction of some element in the sample, considering only primary excitations and a monochromatic beam. There is an equation similar to this for each element in the sample. There are a few standard ways to transition from a monochromatic beam to a polychromatic incident beam. One is by breaking the spectrum up into a number of approximately monochromatic beams or, in other words, dividing the spectrum into small energy bins, each bin approximately representing a monochromatic photon beam. A term such as that described in eq. (2.40) is then used for each of these "monochromatic" pieces of the spectrum. Another option is to make the $I_0$ term in eq. (2.40) a differential ($dI_0 = \eta(E)dE$), where $\eta(E)$ is the probability density function of the spectrum and $E$ is the photon energy. The resulting equation is then integrated over the whole spectrum of energies. Of course, one must know the spectrum to employ these methods, which is not always possible.

Additions to eq. (2.40) are needed to properly describe experimental conditions. Representing the total number of characteristic photons detected by eq. (2.40), assumes that the detector efficiency is 100 % and that there is no absorption by the medium surrounding the sample. Absorption by air and the beryllium detector cov-
erging is accounted for in this analysis. Detector efficiency, which is tied to the probability of photons passing through the detector or the occurrence of escape peaks, is not considered here.

2.6.2 Secondary Excitations

In eq. (2.40) for the intensity of emission of a line $i$, no mention of the other elements in the sample is made. As it stands, this equation does not incorporate any of the absorption/enhancement effects that are ever-present when carrying out X-ray spectrometry on multi-atom samples. The incorporation of this effect is highly necessary as secondary excitations can contribute up to 20 % of the observed peak intensities [22]. What needs to be done is to add a term to eq. (2.40), which itself carries over unchanged. The term is determined by applying the same ideas used for describing excitation by a monochromatic source to the situation depicted in fig. 2.6. The analysis discussed in this thesis uses only primary and secondary excitations; however, this process can be continued, considering higher order excitation effects. The third order effect, tertiary excitation, can contribute a few percent to observed peaks [22]. The higher order terms become less and less important and involve more and more computing time.

![Figure 2.6: Sample geometry for secondary excitation](image)

To describe the secondary excitation peak intensity, $I_{i,sec}$, for analyte line $i$ emit-
ted by the analyte atom, photons emitted by some other, secondary, element in the matrix are considered. A secondary element may emit several different characteristic photons, and all of them must be considered. Any one of these will be labelled as the ‘jth’ emitted photon. For brevity, in the following equations j is used to denote all quantities relating to the secondary element; such as the element, shell and emission line (the context will clarify the exact meaning). The jth photon must be included only if it is sufficiently energetic as to be able to remove an electron from the relevant shell of the analyte atom. The number of photons of type j emitted in the layer dx at depth x in the sample is as shown in eq. (2.37), but with j’s in place of the i’s.

\[ dI_{j,em,dx} = I_{reaching} - dx \omega_j R_j g_j (\mu_{j,E_0} \rho C_j) \frac{dx \sin \phi}{\sin \Phi} = \omega_j R_j g_j (\mu_{j,E_0} \rho C_j) I_0 e^{-\mu_{M,j} \rho (x-y) \sin \theta} dx \sin \phi \] (2.41)

The intermediate step is to determine how many of these photons reach the layer dy and excite the analyte atoms in that layer. This is expressed using the following equation:

\[ dI_{j,\text{reaching}-dy} = dI_{j,em,dx} e^{-\mu_{M,j} \rho |y-z| \sin \theta} \frac{d\Omega'}{4\pi} \] (2.42)

and accounts for the attenuation of the jth emitted photons towards dy, as well as the differential solid angle \((d\Omega' / 4\pi)\) covering dy.

A modification of eq. (2.37) gives the intensity of characteristic photons i emitted by analyte atoms at dy, resulting from the interactions of the photons of type j in that region. This modification is described as follows:

\[ dI_{i,em,dy} = dI_{j,\text{reaching}-dy} \omega_i R_i g_i \mu_{i,j} \rho C_i \frac{dy}{\sin \theta} \] (2.43)

To reach the final differential form of the relation for secondary excitation, the attenuation of the type i photons emitted at y by the matrix, prior to reaching the detector,
must be accounted for. The detector solid angle $\frac{\Delta \Omega}{4\pi}$ must also be considered. This leads to the following result:

\[
dI_{i, \text{sec, reach} - \text{detector}} = dI_{i, \text{em, dy}} e^{-\frac{\mu_{M,i} \rho_y}{\sin \psi}} \frac{\Delta \Omega}{4\pi} \\
= dI_{j, \text{reaching} - \text{dy}} \omega_i R_i g_i \mu_{i,j} \rho C_i \frac{dy}{\sin \theta} e^{-\frac{\mu_{M,i} \rho_y}{\sin \psi}} \frac{\Delta \Omega}{4\pi} \\
\times \frac{dy}{\sin \theta} e^{-\frac{\mu_{M,i} \rho_y}{\sin \psi}} \frac{\Delta \Omega}{4\pi} = \omega_j R_j g_j (\mu_{j,E_0} \rho C_j) I_0 e^{-\frac{\mu_{M,j} \rho_x}{\sin \phi}} \frac{dx}{\sin \phi} e^{-\frac{\mu_{M,j} \rho_y}{\sin \psi}} \frac{d\Omega'}{4\pi} \\
\times \omega_i R_i g_i \mu_{i,j} \rho C_i \frac{dy}{\sin \theta} e^{-\frac{\mu_{M,i} \rho_y}{\sin \psi}} \frac{\Delta \Omega}{4\pi} \\
= I_0 \omega_j R_j g_j \mu_{j,E_0} \rho C_j \omega_i R_i g_i \mu_{i,j} \rho C_i e^{-\left(\frac{\mu_{M,j} \rho_y}{\sin \psi} + \frac{\mu_{M,i} \rho_y}{\sin \psi}\right)} \rho x \\
\times e^{-\left(\pm \frac{\mu_{M,j}}{\sin \theta} + \frac{\mu_{M,i}}{\sin \psi}\right) \rho y} d\Omega' \frac{d\Omega}{4\pi} \frac{dx dy}{\sin \phi \sin \theta} \quad (2.44)
\]

The integration of eq. (2.44) over all $x$, $y$ and $d\Omega'$ yields:

\[
I_{i, \text{sec}} = \left( \frac{I_0 g_i C_i R_i \omega_i \csc \phi}{\mu_{M,E_0} \csc \phi + \mu_{M,i} \csc \psi} \right) \frac{\Delta \Omega}{4\pi} \times \frac{1}{2} \sum_j \left( C_j g_j R_j \omega_j \mu_{i,j} \mu_{j,E_0} \right) \\
\times \left[ \frac{1}{\mu_{M,E_0} \csc \phi} \ln \left( 1 + \frac{\mu_{M,E_0} \csc \phi}{\mu_{M,j}} \right) + \frac{1}{\mu_{M,i} \csc \psi} \ln \left( 1 + \frac{\mu_{M,i} \csc \psi}{\mu_{M,j}} \right) \right] \quad (2.45)
\]

Adding eq. (2.40) for primary excitations to the above equation leads to the final result for the intensity of emission line $i$, considering both primary and secondary excitations, shown in eq. (2.46).

\[
I_{i, \text{reaching} - \text{detector}} = \\
\left( \frac{I_0 g_i C_i R_i \omega_i \mu_{i,E_0} \csc \phi}{\mu_{M,E_0} \csc \phi + \mu_{M,i} \csc \psi} \right) \frac{\Delta \Omega}{4\pi} \left( 1 + \frac{1}{2 \mu_{i,E_0}} \sum_j \left( C_j g_j R_j \omega_j \mu_{i,j} \mu_{j,E_0} \right) \right) \\
\times \left[ \frac{1}{\mu_{M,E_0} \csc \phi} \ln \left( 1 + \frac{\mu_{M,E_0} \csc \phi}{\mu_{M,j}} \right) + \frac{1}{\mu_{M,i} \csc \psi} \ln \left( 1 + \frac{\mu_{M,i} \csc \psi}{\mu_{M,j}} \right) \right] \quad (2.46)
\]
2.6.3 Determining Concentrations

Equation (2.46) gives the intensity $I_i$ if the concentrations of all elements and initial beam intensity are known. The concentrations are what needs to be determined, but since they cannot be solved for algebraically, a procedure is needed to determine concentrations given the set of spectral lines $I_i$’s and the incident beam intensity. The procedure given in [22] has been used. It employs eq. (2.46). This procedure is iterative whereby a guess of the element concentrations is made: eq. (2.46) is used to calculate the peak intensities that would result from the guessed concentrations; these calculated intensities are compared to the measured peak intensities; the initial guess is modified based on how close the calculation is to the measured value; a new guess is made, and this continues until the change in each successive guess is negligible compared to the experimental uncertainty in the concentration.

The guess for each element in the steps described above is modified such that:

$$C_i' = \frac{I_{i,\text{meas}}}{I_{i,\text{calc}}} C_i$$  \hspace{1cm} (2.47)

where $C_i$ is the current guess leading to the calculated intensity $I_{i,\text{calc}}$, and $C_i'$ is the new guess resulting from the comparison between $I_{i,\text{calc}}$ and the measured intensity $I_{i,\text{meas}}$. Prior to the start of the next iteration, the set of $C_i'$ are normalized to one. This procedure removes any dependance of the determined concentrations on any constants applied to all the $C_i'$, such as a constant incident beam intensity. For a polychromatic beam, a calculation like eq. (2.46) must be done for each component of the beam. The results are then summed to give $I_{i,\text{calc}}$. Many of the variables in these fundamental parameters equations (eq. (2.40) and eq. (2.46)) are highly dependent on the element and photon energy, and must therefore be varied as needed. For example, the mass absorption coefficients, which have a dependence on photon energy similar to the photo-absorption cross section in eq. (2.20).
The data used towards results presented here have been sourced from [20], [30], [31] and [21]. Much of this data consists of discrete measurements of the various quantities, and it was generally necessary to interpolate between them to approximate the desired value for a given quantity. A simple, linear interpolation has been used in all cases. Given the small separation of the data in such cases, any deviations from the true values are considered negligible, since they are small compared to other sources of uncertainty.

2.7 VESPERS: Experimental Set Up

VESPERS is a hard X-ray beamline at the Canadian Light Source in Saskatoon, Canada. It is fed by a bending magnet, covering energies in the range of $6 - 30$ keV with a resolution of $\Delta E/E = 10^{-4}$. The VESPERS beamline is capable of both polychromatic and monochromatic beams, with spot sizes down to $2 - 4$ $\mu m$ by $2 - 4$ $\mu m$. The endstation is equipped with $N_2$ filled ion chambers to monitor fluctuations in incident beam intensity, and solid state Si detectors for X-ray Fluorescence detection. The sample stage is not under vacuum, and relevant corrections for X-ray absorption in air must be applied to data. The position of a sample’s surface is monitored by a laser as to keep it in the focus of the incident X-ray beam. Samples are held with their faces at 45° with respect to the incident beam to minimize scattering background at the detectors. The detectors are placed between 45° and 50° with respect to the incident beam. Detector dead time, ion chamber output and other relevant details are recorded for all data sets.
Chapter 3

Analyses

Normalization to the incident beam intensity and dead time corrections are applied to all data sets. This is always necessary as both fluctuate dramatically during data collection, as shown in fig. 3.1. The incident beam intensity varies due to the exponential decay of the electron beam in the storage ring. Variations in the detection dead time are due to fluctuations in beam intensity and sample composition. All fitting of data is done using the ROOT graphical software package [32], unless otherwise specified.

Figure 3.1: (a): Decay of the incident beam intensity with map point (\(\sim 1 \text{ s/point}\)) during data collection on a hadrosaur sample. See fig. 3.2. (b): Dead time variation as a function of map point, in the same map. It is highly dependent on the sample region.
3.1 Mapping

The VESPERS beamline facilitates the making of “element maps” on small regions of samples. A set of cartesian coordinates can be specified for this situation, where \( \hat{z} \) will be defined as the direction of the incident beam, \( \hat{y} \) will be taken as vertically upward from the incident beam and \( \hat{x} = \hat{y} \times \hat{z} \). This will put the \( \hat{x} \) axis parallel to the sample surface, which will then be at 45° with respect to the \( \hat{y} \) and \( \hat{z} \) directions.

With a step motor moving the sample in steps ranging from five to thirty microns in the horizontal (\( \hat{x} \)) and vertical (\( \hat{y} \)) directions, X-ray fluorescence spectra are taken in a grid over the sample surface. With the high beam flux from a polychromatic beam, only 1 s is needed per point in order to collect a statistically significant number of events (\( \sim 10,000 \)). This allows the detailed, micron scale mapping of regions on the order a few square millimetres.

A finished map data set consists of a few thousand fluorescence spectra. In order to create the element maps, a measure of the intensity of the emission lines composing each spectrum is needed. This is done by summing the events in bins within \( \pm 50 \) eV of the nominal energy of each emission line. This width in energy is equivalent to about \( \pm 1\sigma \) for the Gaussian emission peaks, which generally excludes the emissions from nearby emission lines. The background level is relatively low in these spectra, but can be relevant for weak lines. When needed, the background contamination is estimated and removed with an algorithm provide by ROOT, which is based on the SNIP (Sensitive Nonlinear Iterative Peak clipping) algorithm ([26] and references therein).

A two dimensional histogram of the peak intensity for a given emission line at each point in the xy-grid is made. In the first approximation, this peak intensity is linearly related to the concentration of the element corresponding to the observed emission line. However, absorption-enhancement effects and neighbouring peaks from other elements in the same region of the sample can cause deviations from this.
Therefore, in the first approximation the bin contents of each element map will be related to one another as the element’s concentrations in the corresponding regions.

In some cases, visual microscope images of the sample surface are taken in regions corresponding to map locations. Using the software package ImageJ [33], the chemical maps are transposed onto the microscope images. In this way, chemical and visual features of the samples can be correlated. A small correction is made to the image sizes to account for the incline of the sample with respect to the incident photon beam. This is necessary as the microscope camera’s face is parallel to the sample surface.

### 3.1.1 Identifying Minerals

The elements present in samples are generally bound up in minerals. These minerals are characterized by definite fractions of elements present, and by lattice structures. In addition to the nominal elements, all minerals of natural origin might have trace elements present in amounts that may or may not be well defined. A histogram of the peak intensities from an elemental map, in the form # of \textit{map points} vs peak intensity, can be used to identify the presence of individual minerals as well as trace elements. Characteristic peaks should be expected for major elements in the minerals. Peaks for trace elements are not always identifiable. An example for the Ca distribution in a harosaur sample is given in fig. 3.2.

The peaks in these histograms can be fit using a functional form, and all spectra in the map corresponding to a peak (within \(1\sigma\) of the mean) can be averaged. This both improves statistics and creates a mean spectrum characteristic of a mineral or feature in the sample. These spectra are ideal for fitting and putting through an algorithm to determine element concentrations.
3.1.2 Analyzing Spectra

The fitting functions for the X-ray fluorescence spectra have two parts. The first part is a sum of Gaussian peaks, each of which has a three parameters: $a_i$, $b_i$, and $c_i$, associated with it as in eq. 3.1.

$$f_0(x) = \sum_{i=1}^{N} a_i e^{\frac{1}{2} \left( \frac{x-b_i}{c_i} \right)^2}$$ (3.1)
where $b_i$ is the peak centre and $c_i$ the respective standard deviation. The variable $x$ is the measured photon energy. The number of peaks, $N$, and their approximate locations are initially determined by a peak finding algorithm provided by the ROOT software package. The algorithm is based on a deconvolution method ([34]), which improves peak resolution, and applies methods in [35], [36] and [37] to identify the peaks themselves.

The form of the background is determined by the SNIP-based algorithm mentioned above (section 3.1.1). The algorithm iteratively scans the bins in the histogram of the spectrum, comparing the value of each bin to the average value of two bins at a distance $\pm p$ from the current bin. The value of the current bin is replaced by whichever is minimal, the current value, or this bin average. The size of $p$ is chosen in accordance with the width of the peaks and was typically on the order of a standard deviation of the Gaussian emission peaks. The overall effect of this algorithm is to strip the spectrum of its peaks, leaving only the background. This remaining background spectrum can then be used in fitting the original spectrum.

Denoting the fixed background $f_1(x)$, the functional form used to describe the spectra is then:

$$f(x) = f_0(x) + f_1(x)$$

The determined parameters of $f(x)$ are used to determine the area of each peak, $A_i$, in the spectrum. The area is taken to be the integral over all energies of the determined gaussian. These peak areas are taken to be the intensity of each emission line emitted into the element of solid angle subtended by the detector. Prior to use in the concentration determination methods outlined above, a few corrections must be made to the peak areas. Since the VESPERS endstation is not under vacuum, a correction for attenuation by air must be made to the peak intensities. This is accomplished through a transmission coefficient $T_{\text{air}}(l)$, where $l$ is the detector-sample separation. Absorption by the Be detector covering is also relevant, and is incorporated with
another transmission coefficient $T_{Be}(l')$. The thickness is $l' = 12 \mu m$ for all data sets. The values of these coefficients are taken from data tabulated in [20]. These resultant intensities

$$I_i = \frac{A_i}{T_{air}(l)T_{Be}(l')}$$

can then be used to determine element concentrations as described above.

3.2 Effective Beam Spectrum

3.2.1 Method

To determine element concentrations with the Fundamental Parameters method, the energy and relative intensity of all incident photons must be known; that is, the incident beam spectrum. With the beamline’s high energy resolution monochromatic beams, this is not essential, but not so for the polychromatic beam. The polychromatic beam spectrum is not recorded for the VESPERS beamline, which causes a fundamental problem when determining element concentrations. An alternative would be to place some low Z ($Z < 15$) material in the path of the incident beam. Some photons from the beam would scatter off the material and travel towards the detector, without adding detectable fluorescence peaks. However, due to the surrounding air, low energy portions of the spectrum may be attenuated below detection limits. This could have been mitigated by installing the system in a vacuum chamber. Assuming all the above details could be dealt with, it would be necessary to measure the beam spectrum for almost every set of measurements on the beamline, since there is no guarantee that the spectrum would remain unchanged with time. Other alternatives would face similar problems. It is clear that whatever alternative is selected, it would involve various costs, technical complexities and it would also be time consuming. However, an alternate method can be used, which is not time consuming and does
not require the introduction of additional devices or electronics to the beamline.

The intensity of an emission line can be reproduced in several ways. A given emitted intensity resulting from excitations by a polychromatic beam can always be replicated by an effective monochromatic beam. By adjusting the intensity and/or energy of the effective monochromatic beam, the same result for that particular emission line as for the polychromatic beam can be achieved [22].

In the case of a polyatomic sample, with multiple emission lines of interest, the situation is more complicated. The effective monochromatic beam that will replicate the effect of the polychromatic beam for one element, will not necessarily work for another element in the sample. This is a result of the photo-absorption cross sections, which vary with atomic number. A particular emission line intensity, observed in a XRF spectrum, depends on the intensity of the beam over the range of energies capable of exciting it. It is, therefore, imperative that this intensity is known in order to calculate the unbiased concentration of the element associated with that emission line. The solution proposed in this thesis is to find an effective polychromatic beam spectrum composed of $N$ perfectly monochromatic beams, each of them allowed to affect only one of the atoms in the sample.

This situation can be described by a slight modification of eq. (2.46), such that

$$I_{i, \text{reaching-detector}} =$$

$$\left( \frac{g_i C_i R_i \omega_i \mu_{i,E_0} \csc \phi}{\mu_{M,E_0} \csc \phi + \mu_{M,j} \csc \psi} \right) \frac{\Delta \Omega}{4 \pi} \left( I_{0,i} + \frac{1}{2 \mu_{i,E_0}} \sum_j I_{0,j} (C_j g_j R_j \omega_j \mu_{i,j} \mu_{j,E_0}) \right)$$

$$\times \left[ \frac{1}{\mu_{M,E_0} \csc \phi} \ln \left( 1 + \frac{\mu_{M,E_0} \csc \phi}{\mu_{M,j}} \right) \right] \frac{1}{\mu_{M,j} \csc \psi} \ln \left( 1 + \frac{\mu_{M,i} \csc \psi}{\mu_{M,j}} \right) \right] \right) \right)$$

$$\text{(3.3)}$$

where $I_{0,i}$ is the intensity of the $ith$ monochromatic beam affecting only the $ith$ element. If the set of $N$ beams is known, the concentration of the $ith$ element can be determined through the iterative method given above (eq. (2.47) and related text).
To determine the effective beam spectrum, a standard (reference sample) is needed. The standard must have known concentrations of several elements. The primary standard used in these studies is Standard Reference Material 610 (SRM 610) from the National Institute of Standards and Technology (NIST) [27]. Any sample with a set of known element concentrations could be used, though ideally it should be similar in its properties to future analytes. SRM 610 is a glass matrix impregnated with 61 elements with concentrations ranging from $100 - 500 \, mg/kg$. The standard is a circular wafer that is $3 \, mm$ thick. The wafer has a diameter of $12 - 14 \, mm$.

The element concentrations (mass fractions) are guaranteed to varying degrees. There are fifteen certified elements, whose concentrations are given with a high degree of confidence. Two reference values are given. These are not certified, but are best estimates which do not meet the certification criteria. Information values are given for seven elements. These are values considered of interest, but uncertainties were not able to be determined [28]. In this analysis, the uncertainties of the information value mass fractions are taken at twice the mean standard deviation of the certified and reference values. A systematic error based on this assumption is also included. The elements composing the glass matrix are not included in this classification. The matrix is specified as having mass fractions: 72 % $SiO_2$, 14 % $Na_2O$, 12 % $CaO$ and 2 % $Al_2O_3$. Errors for these concentrations are assigned at $2\sigma$. The sample is manufactured to give $\leq 2 \, %$ relative repeatability with the illumination of the full wafer. The data for this analysis was collected as a single point (not a large area map), with a beam spot (diameter) $\leq 10 \, \mu m$. Some deviations from the nominal concentrations might occur at this small scale. However, it should be noted that incident photons with energies ranging from $6 - 30 \, keV$ will have attenuation lengths ranging from $\sim 20 - 2500 \, \mu m$ ([20]). A minimum volume on the order of $1600 \, \mu m^3$ will generally be illuminated, meaning that only inhomogeneities on this scale should
be influential.

To calibrate the effective beam, the element concentrations as given by NIST are treated as known constants in eq. (3.3). Applying the iterative adjustments given in the equation below

\[ I_{0,i} = I_{i,measured} \frac{I_{i,calc}}{I_{0,i}} \]  

(3.4)

the effective monochromatic beams \( I_{0,i} \), where \( i \in \{1, \ldots, N\} \), are determined, resulting in an effective beam spectrum. The term \( I_{0,i} \) is the effective beam for the newest iteration and is based on the \( I_{0,i} \) from the previous iteration. \( I_{i,measured} \) and \( I_{i,calc} \) are the measured (and corrected) peak intensity and the intensity determined using eq. (3.3), respectively. The beam energy is fixed at 18995 eV. This energy was chosen such that the photon interaction cross sections of the various elements will be similar and at the same time, the assumption that \( \sigma \approx \tau \) remains valid [20]. Increasing the intensity and moving the energy closer to the photon-absorption edge have the same effect. Thus, only one of these actions is needed.

The result is a set of \( N \) monochromatic beams, one for each of the elements detected in the sample. Figure 3.3 depicts the spectrum obtained for SRM 610. The elements in fig. 3.3 are a subset of the elements in the sample. They are elements

![Figure 3.3: The effective beam spectrum determined from SRM 610. Intensities are given relative to that of the Sr Kα line.](image-url)
with defined concentrations and Kα emission lines in the detectable energy range ($\sim 2 - 16$ keV). The method could just as well be applied to other shells.

It was expected that the effective beam spectra for different samples should show the same general trend, since absorption/enhancement effects are being corrected for. This is what is observed. There is general agreement among results for elements common to SRM 610 and other reference samples. Some differences between samples are expected in that the real beam spectrum 'seen' by different parts of the sample depends on its composition and thickness. As the incident beam passes deeper into the sample, certain photons of given energies will be selectively absorbed. The side effect of this is that some energy regions of the original spectrum of the photon beam might be attenuated. Therefore, an atom of one type in a particular position in the sample might be excited by photons with a different photon beam spectrum compared to the one which originally entered the sample or even from that reaching different parts of the sample. If the incident spectrum at the sample’s surface were known, this effect would be accounted for in the excitation equation analogous to eq. (2.46), provided an iterative concentration determination method such as eq. (2.47) is used. For this reason, the best result will be expected when the calibration standard and analytes are similar in their absorption/enhancement properties.

### 3.2.2 Functional Form and Fitting Data

A general trend appears in the effective beam spectrum peaks; therefore, it is reasonable to fit it with a functional form for application to all detectable elements. Only K-shell emissions will be considered. A functional form can be obtained by considering the detected intensity in the first approximation where only primary excitations are considered. It is further assumed that the incident photon beam spectrum can be described by a normalized distribution $P(E)$, and by a constant intensity $I_0$, over the incident photon energy range $[E_{\text{min}}, E_{\text{max}}]$. The energy $E_{\text{min}}$ is the minimum photon
energy required to produce the photo-absorption process in the shell of interest. Using the integral form of eq. (2.40) for a continuous incident spectrum, the detected intensity for line $i$ is given by:

$$I_{i,\text{detected}} = \int_{E_{\text{min}}}^{E_{\text{max}}} I_0 P(E) \left( \frac{g_i C_i R_i \omega_i \mu_{i,E} \csc \phi}{\mu_{M,E} \csc \phi + \mu_{M,i} \csc \psi} \right) \frac{\Delta \Omega}{4\pi} dE$$ (3.5)

The variables $g_i$, $C_i$, $R_i$, $\omega_i$, $\mu$, $\Delta \Omega$, $\phi$ and $\psi$ are as defined in chapter two. The monochromatic effective beam for element $i$, represented by $I_{e,i}$, is related to the detected intensity, $I_{i,\text{detected}}$, through the following expression:

$$I_{i,\text{detected}} = I_{e,i} \left( \frac{g_i C_i R_i \omega_i \mu_{i,e} \csc \phi}{\mu_{M,e} \csc \phi + \mu_{M,i} \csc \psi} \right) \frac{\Delta \Omega}{4\pi}$$ (3.6)

The subscript $e$ denotes the effective beam energy. The intensity of the effective beam must be such that $I_{i,\text{detected}} = I'_{i,\text{detected}}$. Equating eq. (3.5) and eq. (3.6), and cancelling terms as appropriate, gives:

$$I_{e,i} \frac{\mu_{i,e}}{\mu_{M,e} \csc \phi + \mu_{M,i} \csc \psi} = \int_{E_{\text{min}}}^{E_{\text{max}}} \frac{I_0 P(E) \mu_{i,E} dE}{\mu_{M,E} \csc \phi + \mu_{M,i} \csc \psi}$$ (3.7)

The mass absorption coefficients are taken to have the form given by eq. (2.19) and eq. (2.26). After substitution into eq. (3.7), solving for $I_{e,i}$ and cancelling terms, the result is:

$$I_{e,i} = I_0 \left( k_{e} \frac{7/2 \csc \phi + k_{i} \frac{7/2 \csc \psi}}{E_{\text{max}} \csc \phi + k_{i} \frac{7/2 \csc \psi}} \right) \int_{E_{\text{min}}}^{E_{\text{max}}} \frac{P(E) dE}{E^{7/2} \csc \phi + k_{i} \frac{7/2 \csc \psi}}$$ (3.8)

Here, one can use that $\phi \approx \psi$, allowing the cancellation of these terms. Alternatively, these terms could have been left in the general case without altering the discussions.

The form of $P(E)$ can be related to the general synchrotron radiation spectrum for a bending magnet, which is described by eq. (2.11) ([17]). Integrating eq. (2.11)
over all angles, as shown in [17], yields the following result:

\[
I(E) \propto \frac{E}{E_c} \int_{E_c}^{\infty} K_{5/3}(x) dx \tag{3.9}
\]

which can be substituted for \( P(E) \) in eq. (3.8). Constant terms left after the integration of eq. (2.11) would either have been absorbed by the factor \( I_0 \) in eq. (3.8) or removed by the normalization conditions in the concentration determination procedure using eq. (2.47). \( E_c \) is the critical energy of the synchrotron, which is related to the critical frequency shown in eq. (2.13), such that \( E_c = \hbar \omega_c \). The critical energy at the CLS is \( \sim 7.6 \text{ keV} \) [39]. The term \( K_{5/3} \) is another modified Bessel function of the second kind, as shown in [17]. This result gives the standard form for the produced synchrotron radiation shown in fig. 3.4.

The spectrum given in eq. (3.9) can be attenuated by the interactions between photons in the beam and objects encountered prior to or in the sample. This feature has to be incorporated into the description of the spectrum expressed by (3.4). In particular, the beamline optics, ion chambers, beam filters (metal sheets used to attenuate the beam for the express purpose of reducing the incident beam intensity) and any air or other gases that must be traversed have to be considered. All of these features are present at VESPERS. To account for this attenuation of the beam, a factor \( T(E)^t \) is used. \( T(E) \) is taken to be the transmission of X-rays by 10 cm of air (nominally \( N_{1.562}O_{0.42}C_{0.0003}Ar_{0.0094} \), at a pressure of 760 torr and temperature of 295 K) as a function of the photon energy, as given by [20]. The power \( t \) is a parameter that can be tuned to best reproduce the attenuation effect. The general form of this beam attenuation is the same regardless of the material under consideration. Therefore, it is a good approximation to describe the attenuation produced by a material by considering the equivalent process for an effective distance travelled by the photon beam in air. The effect of the transmission coefficient is represented by
the red full line in fig. 3.4, showing the effect of attenuation by 10 cm of air, which is described in the general case by eq. (3.10).

\[ I(E) = T(E)E \frac{E}{E_c} \int_{E_c}^{\infty} K_{5/3}(x)dx \]  

(3.10)

It can be seen that the attenuation is more significant at lower energies. The consequence of this attenuation is that the minimum energy of the spectrum is shifted towards higher energies.

![Normalized synchrotron radiation spectra](image)

Figure 3.4: Normalized synchrotron radiation spectra as described by eq. (3.9). The graph shows normalized intensity as a function of energy in eV. The black curve shows the original spectrum. The red curve shows the spectrum after attenuation by 10 cm of air [20]. (Original In Colour)

The final functional form for the effective beam intensity can be reached by using eq. (3.9) and the attenuation factor \( T(E) \); eq. (3.8) then gives

\[ I_{e,i}(k_i, E_{edge}) = I_0 \left( k^7_{e} + k^7_{i} \right) \int_{E_{edge}}^{E_{max}} \frac{T(E)E}{E_c} \int_{E_c}^{\infty} K_{5/3}(x)dxdE \]  

(3.11)

where it is assumed that for a given element \( i \), the value of \( E_{min} \) is always equal to \( E_{edge,i} \). Only photons with energy greater than, or equal to, \( E_{edge,i} \) can be photo-absorbed.

The powers of the photon energies in eq. (3.11) are taken to be parameters,
as is the leading coefficient $I_0$. The former is necessary since, based on eq. (2.20), deviations from the power relationship between $\mu$ and $k$ (see eq. (3.5)) are expected near the absorption edges. It is also assumed that the photon emission and absorption edge energies, as given by [20], can be described by nearly quadratic functions of the atomic number $Z$. Fits to these data show that $E_{\text{edge},i} = (1 \, eV \pm 10 \, eV) + (6.22 \, eV \pm 0.06 \, eV)Z_i^{2.161 \pm 0.002}$ and $k_i = (2 \, eV \pm 12 \, eV) + (6.91 \, eV \pm 0.09 \, eV)Z_i^{2.096 \pm 0.003}$. These values are fixed in the fitting functions described below, as letting both vary results in highly correlated parameters. Taking all the above into consideration, the final fitting function can be written as:

$$I_e(Z) = p_0(k_e p_1 + (a + bZ^c p_1) \int_{\text{E}_{\text{max}}}^E \frac{T(E)^p}{E_e} \frac{E}{E_e} \int_0^\infty K_{5/3}(x) \, dx \, dE} \frac{E^{p_1} + (a + bZ^c p_1)}{(d + fZ^g)}$$

(3.12)

with free parameters $p_j$, with $j \in [0, 1, 2]$.

The importance of the correction for the attenuation of the incident beam, prior to its reaching the sample, in the construction of the effective beam spectrum method is evident when observing its effect in fig. 3.5. Without this correction, the observed form of the effective beam spectrum, as depicted in fig. 3.5(b), cannot be achieved.

### 3.2.3 Fit Results

The result of the fit using eq. (3.12) (represented by red full lines) to the effective beam values (represented by dots with error bars) obtained using the method described in section 3.2.1 is shown in fig. 3.6.a. Figure 3.6.b depicts the values of the relative intensity of the beam for each atomic number, from $Z = 10$ to $Z = 50$, based on the results from this fit (red dots with error bars). The error bars are a combination of those determined from the Chi-square fit method [32] and a systematic error resulting from the assumption of a $2\sigma$ error in those SRM 610 element concentrations without defined uncertainties. The systematic error was derived by fitting the data with errors
Figure 3.5: Relative intensity vs atomic number for effective beam spectra without (a) and with (b) attenuation of the incident photon beam spectrum as given by equations (3.10) and (3.9), respectively. Full line (in red) is the functional form, while circles with error bars are values determined from the data, using the effective beam method. (Original In Colour)

of 1σ and 3σ assigned to the SRM 610 elements without defined uncertainties. The differences between the resultant effective beam intensities \( |I_{1\sigma} - I_{3\sigma}| \) is then taken as the systematic error. Also shown in (b) are the same data points (circles with error bars) as depicted in (a). The corresponding parameter values are found in table 3.1.

Figure 3.6: (a): Fit (red full line) using eq. (3.12) to the points calculated with effective beam spectrum method (dots with error bars). (b): Results from the fit for \( Z = 10 \) to \( Z = 50 \) (red circles with error bars) compared to the data points from the effective beam spectrum calculation (black circles with error bars). The errors on the fit values are the sum of those determined from the Chi-square fit method and the systematic error from assumptions about the magnitude of the uncertainties for some elements. (Original In Colour)
All the element concentration calculations using polychromatic beam data will use, from now on, the corrected effective beam spectrum shown in fig. 3.6, rather than the original polychromatic beam spectrum, as described above. As a test for the consistency of this method, the element concentrations for the SRM 610 sample are reproduced using eq. (3.5) and the calculated effective beam spectrum. The results are compared with those quoted by NIST. There are two variations of the calculation shown in fig. 3.7. The first one compensates for the undetected elements in the sample, which are out of range of energies accessible at VESPERS, by including them in the matrix’s mass absorption coefficient and in the normalization of the concentrations. A reference element is chosen, and all undetected elements are included in their nominal concentrations relative to the reference element. This method will be referred to as the “compensated” method. The other variation uses only detected elements in the calculation, and will be referred to as “non-compensated”. Figure 3.7 shows the results of these calculations. Figure fig. 3.7.a shows that the compensated (open circles with error bars) and nominal (dots with error bars) values agree within errors, with the exception of Cr, $Z = 22$. On the other hand, fig. 3.7.b shows that the non-compensated numbers (red open squares with error bars) are shifted relative to the nominal concentrations (dots with error bars), despite showing the correct trend. This discrepancy arises from normalization of the values. If only a subset of elements is considered, the normalization condition

$$C_{i, normalized} = \frac{C_i}{\sum_{j=1}^{N} C_j} \quad (3.13)$$

<table>
<thead>
<tr>
<th>parameter</th>
<th>value</th>
<th>error</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p_0$</td>
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<td>0.00008</td>
</tr>
<tr>
<td>$p_1$</td>
<td>7.0</td>
<td>0.1</td>
</tr>
<tr>
<td>$p_2$</td>
<td>41</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 3.1: Parameter values for the fit to effective beam data with eq. (3.12).
will result in an apparent increase in the amount of an element present with respect to what is actually there. However, this problem can be mitigated if only relative concentrations are used. In fig. 3.7.c, the concentrations are given relative to the iron concentration. In this case, the non-compensated values have significantly better agreement with the nominal values when compared to the case where only the absolute concentrations are considered. However, there are still a few deviations. These may be due, in part, to small scale variations in the SRM 610 sample. Other aspects will be considered below.

It is critical that there is agreement between the non-compensated and the nominal concentrations, as the non-compensated scenario is the one that matches the general experimental conditions. If agreement exists, the relative concentration values will be reliable for other samples where some fraction of the elements in the matrix might be unknown.

As discussed above the nominal, non-compensated and compensated values generally agree when the data sets are normalized to their respective iron concentrations. The agreement is better with the non-compensated results than the compensated in some instances, though the converse is also true as seen in fig. 3.8. The figure shows the deviation of the non-compensated and compensated concentrations from the nominal values as a function of atomic number. It is seen that at the extremes of the range \((Z = 20 \text{ and } Z \geq 34)\), the compensated concentrations provide better estimations of the nominal values. In between these extremes the deviations are similar. In several instances the non-compensate values show better agreement. For example, at \(Z = \{22, 27, 28, 30, 34\}\). This could be expected on the grounds that the compensation method enforces the assumption that a series of elements in the sample are present in certain amounts. All results will be influenced by the validity of this assumption, since it alters the absorption enhancement effects in the sample. The Ca, Rb and Sr concentrations suggest possible deviations from the nominal values.
Figure 3.7: Application of the functional effective beam and fundamental parameters method to SRM 610 data. Both “compensated” (includes un-detected elements from SRM 610) and “non-compensated” (detected elements only) results are shown. (a): Absolute concentration results, showing the general agreement between the compensated and nominal concentrations. (b): Absolute concentration plot using a log-scale. It can be seen that the compensated Ca concentration agrees with the nominal value. (c): Concentrations relative to $C_{Fe}$, the non-compensated values are no longer shifted and show general agreement with the nominal and non-compensated concentrations. (d): Same plot as in (c), but using log-scale. (Original In Colour)

on the scale of the measurement here, especially in the case of the non-compensated concentrations. The Ca concentration may be prone to variation on the scale used here, since it is just a component of the glass matrix. Nonetheless, the compensated determined concentration for Ca agrees with the nominal value. The Rb and Sr more closely take on the nominal trend for the non-compensated calculation. This suggests that for this pair, the true absorption and enhancement effects are better accounted for when no assumptions about the matrix composition are enforced, even though...
they do not numerically agree with the nominal values. The Ca, Rb and Sr concentrations represent the extremes in this scenario and, therefore, help define limits of the method and assumptions being used.

In terms of emission and excitation energies, Rb ($k_{Rb, K\alpha} \sim 13.4 \text{ keV}$, [5]) and Sr ($k_{Sr, K\alpha} \sim 14.2 \text{ keV}$, [5]) are at the high end of the energy scale for this analysis. The approximation that $\tau \gg \sigma_{\text{scattering}}$ is less valid at higher energies [20]. However, a larger effect at this higher energy region is the loss in detection efficiency by about 40% of these emission lines, according to [20]. In the end it is the relative efficiency that matters (eq. (2.47)). Therefore, the efficiency for each emission line must be considered. Interestingly, as the likelihood of photon emissions passing through the sensitive volume of the detector decreases, with decreasing atomic number $Z$ (of the emitter), the likelihood of losses due to the escape peak phenomenon increases [38]. The two will balance each other to some extent. With the current assumptions, these effects cancel each other out to a degree, but if one is considered, the other must be as well.

The Ca concentration represents an extreme of concentration. It is one of the few major constituents of SRM 610. This does not influence the accuracy of the
determined concentration of Ca when all elements are accounted for, as seen in the compensated case (earlier in section 3.2.3). However, the determined Ca concentration does not agree with the nominal one for the non-compensated calculation (section 3.2.3). Since Ca is the only major constituent which is detectable, the effect on the non-compensated calculation is for the sample matrix to be treated as though it was almost entirely composed of Ca. This is, of course, not the case. This does not greatly influence the determined trace element concentrations (fig. 3.8). It follows from eq. (2.19) and the accompanying discussion that the emissions from a group of heavier atoms (here S ($Z_S = 16$) to Zr ($Z_{Zr} = 40$)) will be more strongly attenuated by lighter atoms (here: $Z < Z_S$), the closer their atomic numbers are to that of the heavier atoms (here: $Z \rightarrow Z_S$). Therefore, Si attenuates Ca emissions more strongly than does B, for example. Using Ca as an example, for $Z_{\text{matrix}} \ll Z_{\text{Ca}}$ the matrix will be almost transparent to the Ca-$K\alpha$ emissions ($Z_{\text{matrix}}$ is the effective atomic number of the matrix). For a matrix with considerable Ca ($Z_{\text{Ca}} = 20$) and K ($Z_K = 19$) present, the K will strongly influence the Ca emissions. This follows from eq. (2.19), as mentioned, but is also verified by data in [20]. As the concentration of K decreases (K is replaced by something lighter), the matrix will become more transparent to the Ca emissions. That is why the Ca concentration is prone to deviations from the nominal value in the non-compensated result. In the compensated case, the matrix is composed of mostly light elements. To the emissions of all the elements in the group of interest, S to Zr, the matrix is semi-transparent. In the non-compensated case, the light elements are omitted and the matrix is treated as composed mostly of Ca, changing its relative effect on the emissions of elements in the sample. In most cases Ca will be less transparent to the emissions from the sample, than the actual matrix. Only detecting a subset of major constituents of a sample will generally result in a dramatic shift in the way the matrix is specified in concentration calculations. Since most sedimentary matrices will be composed of light elements, the results for
lighter elements in the detectable range (such as Ca), will often be the most strongly
influenced by variations in how the matrix is specified. The implication is that the
accuracy of the determined concentrations for major components of the matrix will
increase as more of these elements are detected and considered.

Data have been collected for several mineral references. Considered here are
clinopyroxene \((Ca(MgFe)Si_2O_6)\) and biotite \((K(Mg,Fe)_3(AlSi_3O_10)(OH)_2)\) [47].
These are natural samples and, therefore, contain many trace elements in addition to
the nominal ones. The nominal elements are of interest for testing the method, since
to test the determination of trace elements, measurements through another method
must be performed, such that the results of both may be compared. The nominal
ratio of atomic fractions \(C_{Fe}/C_K = 3\) is expected for biotite, while \(C_{Fe}/C_{Ca} = 1\)
is expected for clinopyroxene. From this point forward, concentrations will refer to
atomic fractions as opposed to weight fractions. This will allow for a more straight
forward comparison to the nominal compositions of minerals.

X-ray fluorescence measurements on the biotite reference give \(C_K = 0.28 \pm 0.08\) and \(C_{Fe} = 0.6 \pm 0.1\), for a ratio of \(C_{Fe}/C_K = 2.2 \pm 0.8\). Similarly, for the
clinopyroxene sample it was determined that \(C_{Ca} = 0.51 \pm .13\) and \(C_{Fe} = 0.41 \pm .07\),
yielding a ratio of \(C_{Fe}/C_{Ca} = 0.8 \pm 0.2\). Both of these results agree with expectations
from the nominal mineral compositions. The concentrations are non-compensated.

As with the SRM 610 sample, the relative concentrations agree with the nominal
values without considering undetected elements. It should also be noted that these
samples all represent different matrices, suggesting validity of the method for different
sample types. The matrices of SRM 610 and those of these minerals are similar in
that a considerable portion of each material is composed of low-Z elements, which is
typical of many minerals. In the event that all elements can be detected, the absolute
concentrations should be valid estimates of the real concentrations, and accuracy of
results should improve. General improvement will occur from the improved modelling
of the matrix composition. The absolute concentrations will become more accurate if all elements are detected, as a result of the normalization (eq. (3.13)) being correct.

It is also interesting to note that the clinopyroxene data and biotite data were taken during different runs on the VEPSERS beamline. The biotite and SRM 610 data were taken during the same run. Further the two runs used different XRF detectors. It can be suggested that the effective beam results can be applied across runs. This is assuming that no major change in beamline conditions has occurred that would effect the beam spectrum, such as the insertion of a beam filter, which has been done occasionally.

### 3.3 Application to Samples

The Effective Beam Method, as outlined above, has been applied to a variety of fossil and sediment samples with the aim of determining diagenetic alteration, aspects of the fossilization processes and possible remnants of the original fossil chemistry. The samples are from two Cretaceous formations in western Canada. Hadrosaur and tyrannosaur fossils from the Frenchman Formation (Late Cretaceous) ([42]), near Eastend, Saskatchewan are examined. Also considered are samples from a well preserved hadrosaur discovered in the Wapiti Formation (late Campanian, Cretaceous) of west-central Alberta ([29]; Bell et al., 2013). These samples provide an interesting test ground because they represent different species with potentially, different preservation conditions. All analysis presented is of synchrotron X-ray fluorescence maps of subregions of these samples, unless otherwise specified.

#### 3.3.1 Frenchman Formation Sample Group

The tyrannosaur fossils are from a *Tyrannosaurus rex*. Two bone types are considered: vertebrae and ribs. There are two general types of bone architecture that can be
identified, compact (compacta) and cancellous (spongiosa) [1]. Compact bones are those in which the mineral portion of the bone tissue occupies at least 50% of the volume occupied by the porous space of the bone. Cancellous bones are those where this criterion is not met. The outer cortex of the bone is often compact, becoming spongy toward its interior [1]. Bones may also be classified in terms of the orientation of their Harvesian [1] canals. In longitudinal bone the canals are predominantly aligned parallel to the long axis. Other types are laminar (circumferential canals), plexiform (canals run in multiple directions), reticular and radial [1]. The vertebra sample is a thick section of a porous, spongy bone. There are large cavities inside of the bone, all are at least partially filled with sediment, as seen in fig. 3.9. The sediment inside and outside of the vertebra is a well cemented sandstone of moderately sorted quartz [43]. Thick sections (~1 cm) from two different ribs exhibiting different preservation states are used. The ribs are much denser than the vertebra, and the Harvesian canals are aligned longitudinally. The hadrosaur sample is compact bone and is classified as a piece of vertebra (fig. 3.9).

Figure 3.9: (a): TrexV2.1, a T. rex vertebra section. Several sub-regions are shown where XRF maps have been made. (b): HaV2.1, a section of hadrosaur vertebra. The cross hairs denote the approximate XRF mapping region. (Original In Colour)

Many of the observed features of these samples are exemplified in the T. rex vertebra section, labelled here as TrexV2.1. There are two sub-regions of the sample
being considered; s0 and s1 as shown in fig. 3.10. In the images, the light coloured bone is seen enveloped in a dark sediment layer, in addition to the bulk orange-red sandstone. The multi-layered sediment shows up not only visually, but chemically. Characteristic X-ray fluorescence spectra for important features of these subregions are shown in fig. 3.11. Element maps of the K-shell emissions of S to Zr were made, as were maps for the L-shell emissions of several high atomic number elements such as Ba and Ce.

![Figure 3.10](image1.png)

**Figure 3.10**: (a): Map region s0 from TrexV2.1, outlined in red. (b): Map region s1 from TrexV2.1, outlined in red. (Original In Colour)

![Figure 3.11](image2.png)

**Figure 3.11**: X-ray spectra with Kα emission peaks of elements of interest marked. (a): Characteristic spectra from region s0 in sample TrexV2.1. (b): Characteristic spectra from region s1 in sample TrexV2.1. (Original In Colour)

The maps showing the distributions of Ca, Fe, Mn and Sr in the sample TrexV2.1s1 are shown in fig. 3.12. These elements define the major features of the sample. The
distribution for sulphur (S) (fig. 3.13) indicates that this element is at its highest concentration in the sediment. The map for Mn shows that this element is richer in the dark sediment region, represented by the light blue band through the centre of the map in fig. 3.12. Iron content is also elevated in this region when compared to the bone. The bone shows a higher concentration of Ca, as would be expected for any form of apatite [46]. The dimpled iron distribution indicates iron-rich cement encasing clasts of low-Z elements. Other analysis ([43]), as mentioned, suggest the clasts are predominantly quartz ($SiO_2$), which is supported by what is seen here. It is also apparent that the Sr content is elevated in the bone with respect to the sediments. Strontium replaces calcium in bones ([40], [41]). The observation of the higher Sr content in the bone region of the sample suggests, thus, two possibilities: incorporation into the bone through diet while the animal was still alive; or replacement of Ca by Sr in the bone apatite during diagenesis. It can also be seen that in a small crack in the bone's interior surface, that an exceptionally high strontium region is present (see Ca and Sr maps of fig. 3.12). A preliminary suggestion is a mineral such as barite ($BaSO_4$) [43], or in light of the high Sr content, celestite ($SrSO_4$). The presence of the $SO_4^{2-}$ anion, is possible given the S content of the sediments. Both minerals are white and colourless [47], matching what is seen in some samples (fig. 3.17). Further analysis of this accessory mineral will follow.

The maps showing the distributions of some key elements in the sample TrexV2.1s0 are depicted in fig. 3.14. The Mn map is of particular interest since it suggests four distinct sediment regions. They are the higher Mn interfaces and the bulk sediments inside (bottom of the map) and outside (top of the map) of the bone (regions are labelled in the Mn map of fig. 3.14). The Mn rich interface and high Fe cement of the non-interface sediments are highly suggestive of bacterial action around the fossil bone. This is further suggested by the general presence of S in the sediments surrounding the bone. These are all the elements expected to be present following the
breakdown of organic material by anaerobic bacteria ([15], [16]), and are in keeping with the reaction series discussed above in section 2.1. The burial conditions of this particular specimen are discussed at length in [42]. The presence of elements associated to bacterial activity both inside and outside of the bone suggest the bacteria may have been present in both of these locations during early diagenesis. The presence of sediment grains, as opposed to mere precipitates from the interstitial fluid, in the bone supports the possible fracture of the bone around the time when bacteria were active around the specimen. The excess of free Fe in the interstitial fluids around the fossil led to the precipitation of an Fe rich cement around parts of the fossil. Since the cement elsewhere on the fossil has been determined to be calcite ([42], [43]) it
Figure 3.13: Sulphur (S) distribution in TrexV2.1s1. It can be seen that the S content of the sediment (bottom of the image) is elevated with respect to that of the bone (top of the image). (Original In Colour)

is likely that a mineral such as ankerite has precipitated in this location, supporting what is said in [43].

It should be asked whether a similar trend is observed in the compact rib bones of this tyrannosaur. There are two rib sections that have been studied, each with a slightly different degree of preservation. They are shown in fig. 3.15 and are labelled TrexR1.1 and TrexR6.1, the latter exhibiting “better preservation” in that the small scale structure of the bone is better preserved. Characteristic X-ray fluorescence spectra from each of these samples are shown in fig. 3.16.

Visually, the TrexR1.1 sample shows a few differences when compared to the vertebra discussed above. No dark layers are visible around the bone, and the cement has a grey, rather than orange-red hue. The sediment itself is coarser near the bone, fining with distance from it. This contrasts the relatively fine grains encasing the vertebra. The environment of the rib, near the time of cementation, may have been a higher energy depositional setting than that of the vertebra. It is expected that the exterior sediment here will not exhibit the same elevated Mn and Fe concentrations. This may imply the cementation around the exterior of the bone occurred at a later time, when bacterial activity had reduced.
Figure 3.14: Sample map TrexV2.1s0. (a): Map of Ca $K\alpha$ emissions. (b): Map of Fe $K\alpha$ emissions. (c): Map of Mn $K\alpha$ emissions. Characteristic regions are labelled. They are bands along the width of the map formed by the sediments on the interior and exterior of the sample, high Mn interfaces inside and outside of the bone and the bone itself, which is the low Mn void in the centre of the map. (d): Map of Sr $K\alpha$ emissions. The maps have a $20 \mu m$ by $20 \mu m$ pixel size. (Original In Colour)

Element maps of microscopic regions of these ribs show that there are similarities with the vertebra. Two of the microscopic regions mapped are shown in fig. 3.17. Element maps for these regions of TexR1.1 and TrexR6.1 are depicted in fig. 3.18 and 3.19, respectively. The infilled canals are easily identified as the regions of high Fe and Mn emissions, which form circular shapes in the element maps. The infill has a homogeneous appearance and a bronze colour at this scale ($\sim \mu m$). A pale region is seen along the rim of the Harvesian canal (indicated with red arrows in fig. 3.17) of TrexR1.1. This is a high Sr region analogous to that seen in TrexV2.1s1.

The chemical maps for TrexR1.1 (fig. 3.18) show that there is a clear chemical
Figure 3.15: (a): Image of a section of *T. rex* rib, TrexR6.1. This is a semi-well preserved rib. Structures such as bone osteons are visible in the image without aid of a microscope. (b): Sample TrexR1.1, a section of a different rib from the same animal as TrexR6.1. This sample is still embedded in the host sediment. (Original In Colour)

Figure 3.16: (a): Characteristic spectra from sample TrexR1.1. (b): Characteristic spectra from sample TrexR6.1. (Original In Colour)

distinction between the regions of the sample. It is seen that the Ca concentration is not uniform, but has pronounced Ca hot spots and is clearly diminished in the Harvesian canal. The canal shows elevated Fe, Mn and S. There are no dimples suggesting the presence of sedimentary grains, which is not surprising given the small size of the canals. It could also be that the canals were blocked by bacteria [44], or other minerals [45] that precipitated therein. The chemical makeup mirrors that
of the cement seen in and around the vertebra, suggesting that what is seen here is a precipitate from interstitial fluids that migrated into the canals. This could also represent minerals precipitated from local, bacterially-reduced elements. This chemical makeup along with the visual appearance of the infill mineral suggest an iron sulphide mineral, such as pyrite [47]. Pyrite is a mineral commonly associated with the decay of organic material when sufficient sulfate is present [15]. Fresh water environments often lack the concentrations of sulfate needed for pyrite formation [15], but the introduction of decaying organic material could be a source of extra sulfate [16]. Similar results are seen in TrexR6.1 (fig. 3.19). The precipitate in the canals of the ribs seems to contrast the cement found on the exterior of the ribs. This may suggest a later time of deposition for the sediment around the ribs. The latter deposition event(s) and pore waters apparently did not removed the initial high Fe, Mn, S precipitate from the canals in the bone. Other analysis of this fossil’s depositional setting, [42], suggests burial occurred over an extended period of time. That result is corroborated here. These results also may exclude transport as the cause of different minerals inside and outside of the bone, which may also occur [1]. That the mineral inside of the ribs, in terms of elements present, matches that both
inside and outside of the vertebra from the same location, suggests multiple burial events, not transport.

Figure 3.18: Element emission maps from the interior of the TrexR1.1 sample. Focus is on the osteon shown in fig. 3.17. (a): Map of Ca Kα emissions. (b): Map of Fe Kα emissions. (c): Map of Mn Kα emissions. (d): Map of S Kα emissions. The maps have a 5 µm by 5 µm pixel size. (Original In Colour)

Many of the above features are seen for the hadrosaur sample HaV2.1s1. Characteristic spectra from sub-regions of the sample are shown in fig. 3.20. Maps for the Ca, Fe, Mn and Sr distributions are shown in Figure 3.21. Here, the high Ca emissions mark the bone in the upper quarter of the image and the sediment in the lower left. Once again, the Ca distribution in the sediment is dimpled, suggesting the Ca is part of the cement, which encases assorted low-Z clasts. The Fe and Mn distributions are mirrors of each other. An intense layer of these elements is seen in the midriff of the image, with several plumes percolating up to the bone’s outer edge. In between
Figure 3.19: Element emission maps from the TrexR6.1 sample. Focus is on the osteons shown in fig 3.17. (a): Map of Ca $K\alpha$ emissions. (b): Map of Fe $K\alpha$ emissions. (c): Map of Mn $K\alpha$ emissions. (d): Map of S $K\alpha$ emissions. The maps have a $10 \, \mu m$ by $10 \, \mu m$ pixel size. (Original In Colour)

Figure 3.20: Characteristic spectra from sample HaV2.1s1. (Original In Colour)
the edge of the bone and the highest Fe region is a region of bone fragments. The Fe and Mn are, therefore, surrounding these bone fragments, discernable through their high Ca emissions. The Sr distribution is also noteworthy. Although the bone and sediment are both high in Ca, only the bone shows an elevated Sr content. This is highly suggestive of a biological origin, on the assumption that diagenetic Ca replacement by Sr should effect the cement and bone similarly. A few small points in the sediment appear to have some Sr content, and there is diminished Sr in the bone fragments. The latter suggests the removal of Sr, or an anatomical difference from the main mass of bone. Also possible is that the fragments are very thin and this is an effect of low Sr material underneath the sample’s surface.

Figure 3.21: Element emission maps of the HaV2.1s1 region. (a): Map of Ca Kα emissions. (b): Map of Fe Kα emissions. (c): Map of Mn Kα emissions. (d): Map of Sr Kα emissions. The maps have a 20 µm by 20 µm pixel size. (Original In Colour)

The layering of the different sediment types, as shown in fig. 3.21, may be
suggestive of the time line of burial. Manganese is present closest to the bone, and is the first of the detectable elements in the series of elements reduced by anaerobic bacteria. In the tyrannosaur sample, iron and sulphur occur in a thicker layer that mixes with or succeeds the manganese layer. These elements are more mixed in the hadrosaur sample.

A map of the high Sr emissions from the TrexR1.1 sample is shown in fig. 3.22. Similar mineral features lining canals, or in the cracks of bone samples, are common in those samples mapped to date and are not specific to the Frenchman Formation. They are frequently in the interior of bones as opposed to the exterior. However, this may be an effect of the sample set, which heretofore has had more maps of interior regions. There is a tendency not only towards high Sr, but high Ba and Ce in these regions, as shown in Figure 3.22. Interestingly, both Ba and Ce have biological roles similar to Sr in bones and replace Ca in the bone apatite. As mentioned earlier in this section, a possibility is that S, and here also Ba, might be present in the form of baryte (\(BaSO_4\)). The XRF analyses suggest that the mineral presented in the sample is something similar, but more complex. The prominence of Sr suggests that Strontianite (\(SrCO_3\)) or Celestite (\(SrSO_4\)) are possible. Though its constituents are outside of the detectable range, the presence of the carbonate anions (\(CO_3^{2-}\)), needed for the formation of \(SrCO_3\), could be suspected based on the analysis in [42]. There it is suggested that the river where the specimen was deposited was rich in \(CaCO_3\). The visual homogeneity of the region in TrexR1.1 suggests a composite mineral with both high Ba and Sr, accompanied by several other trace elements. More quantitative analysis shows the high Sr regions in the rib and vertebra are highly similar. The element maps do not elucidate well the S content of these regions, which could be used to differentiate between some of these minerals.
Figure 3.22: (a): A Sr emission map from the TrexR1.1 sample. There is an obvious high Sr emission region corresponding to the pale lining of the canal. (b): XRF spectral region where Ba and Ce L-shell emissions are expected (4 keV ot 6 keV). Shown are the average spectra from the high Sr emission regions of the TrexV2.1s1 and TrexR1.1 samples. (Original In Colour)

### 3.3.2 Wapiti Formation Sample Group

There are two samples used from this location, both are from the same exceptionally preserved hadrosaur specimen. The specimen is from a monodominant hadrosaurine bonebed and was deposited in a freshwater environment [29]. The fossils are deposited in a carbonate-cemented sandstone with low-Z dominated clasts. The area also exhibits organic rich overbank deposits and volcanic bentonite deposits interbedded with coal lenses [29]. One sample is a thick section of a rib (HaR1.1), the other is a thick section of calcified tendon (HaTn1.1). Formation of bone structures in tendons is briefly covered in [1]. They are shown in fig. 3.23. It is immediately apparent, when looking at the tendon sample, that the interior and exterior sediments are of a different nature. Elemental analysis shows the same for the rib. Characteristic X-ray fluorescence spectra are shown in fig. 3.24

Element maps for the rib and tendon (figs. 3.25 and 3.26, respectively) demonstrate unique burial conditions for this hadrosaur specimen. It is evident that the chemical makeup of the sediment in the canals is very different from that of the Frenchman Formation samples discussed above. The bone is still higher in Ca than
Figure 3.23: Samples from the Wapiti Formation. (a): Section of hadrosaur rib, HaR1.1. (b): Section of calcified hadrosaur tendon, HaTn1.1. A small fragment of marbled, grey sediment is attached to the exterior of the tendon. This sediment is indicative of the sediments of the area. The samples, as shown, have heights of \( \sim 1 \text{ cm} \). (Original In Colour)

Figure 3.24: (a): Characteristic spectra from sample HaTn1.1. (b): Characteristic spectra from sample HaR1.1. (Original In Colour)

the mineral infilling the bone. However, the Fe, Mn and S emissions are at their most intense in the bone as well. They are not necessarily at higher concentrations than in the Frenchman T. rex bones, but they are certainly at greater concentrations relative to the bone infill. This is the opposite of what has been found for the fossils from the Frenchman Formation. All the elements shown are seen to vary in the same way, suggesting most are incorporated in amounts proportional to major bone constituents.
(such as Ca). The fluctuations potentially being due to bone mineral density.

The sediments exhibit very low emissions for all elements in the detectable range, suggesting a relatively pure mineral of low-Z elements. Carbonates are good candidates, and suggest that the infill is a precipitate of the pore interstitial fluids that cemented the sandstone in the area at large. Of particular interest is that few elements associated to bacterial action are present in the infill, whereas in the Frenchman samples the infill was dominated by such elements. This may simply suggest replacement of the bacterial products. However, the burial conditions of the location in question are unquestionably unique, since they have fostered the exceptional preservation of hadrosaur skin. Such exceptional preservation is always suggestive of special diagenetic conditions [16]. It can be suggested that the lack of bacterial products is due to

Figure 3.25: Element maps for the HaR1.1 sample. (a): Map of Ca Kα emissions. (b): Map of Fe Kα emissions. (c): Map of Mn Kα emissions. (d): Map of S Kα emissions. The maps have a 15 µm by 15 µm pixel size. (Original In Colour)
Figure 3.26: Element maps for the HaTn1.1 sample. (a): Map of Ca $K\alpha$ emissions. (b): Map of Fe $K\alpha$ emissions. (c): Map of Mn $K\alpha$ emissions. (d): Map of S $K\alpha$ emissions. The maps have a 15 $\mu$m by 15 $\mu$m pixel size. (Original In Colour)

their inability to enter the canals of the bone, implying the bones were not fractured, or were well sealed, at the time when bacteria (or associated elements) were active around the bone; or there was a lack of bacterial action around the sample; or such action was not able to be captured mineralogically.

It is worth noting that there is evidence of bacterial action in some parts of the fossil. The preserved skin shows high Fe, Mn and S levels around and incorporated into itself. It is also generally accepted that some bacterial activity is necessary for exceptional preservation of soft tissues [16]. A proposed explanation for the preservation of the skin of the specimen is through rapid mineralization, likely catalyzed by bacteria, combined with a reduction in the rate of the organic decay of the animal [29]. In light of the association of Mn, Fe and S with the soft parts of this hadrosaur,
it may be interesting to consider that the high Mn region adjacent to the French-
man Formation samples could be associated to soft tissues as well, hence why it is
segregated from the rest of the sediment. Reduction of Mn, being an earlier stage
of bacterial action, may also support this. During early decay, the high Mn mineral
may have formed around still present soft tissues, which were subsequently lost to
the decay process.

3.3.3 Comparison

A more quantitative discussion of the elemental contents of the above samples is
warranted. In particular, the compositions of the sediment/mineral infills in the
canals of the bones and those of the different bones themselves are of interest. The
histogram method outlined early in this chapter has been used to single out particular
regions of interest in each map. The spectra in the regions are averaged, fit and the
concentrations are determined using the methods described in sections 2.6, 3.1 and
3.2. The errors in the data points (error bars) are determined through differential
error analysis of the relevant equations and through the methods described in those
same sections. The systematic error associated with each measurement will be quoted
separately only when relevant. The values quoted are the atomic fractions, where only
observed elements are considered, unless otherwise specified. Labelling in the figures
is such that: “int” denotes a sediment-bone interface; “in” denotes the interior of the
bone; “ext” denotes the exterior of the bone; and “sed” denotes the sediments away
from the sediment-bone interface. Lastly, the prefixes “l”, “m”, “h” and “v” for the
element names refer to the concentrations of the elements and denote low, moderate,
high and very- respectively. The determined concentrations for several key elements
are given in tables 3.2 and 3.3.

The sediments of the TrexV2.1s0 sample show the general characteristics of
most of the sediments and cement in the Frenchman Formation sample set. The
<table>
<thead>
<tr>
<th>Sample - Region</th>
<th>$C_{Ca}$</th>
<th>$C_{Mn}$</th>
<th>$C_{Fe}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TrewV2.1s0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>hMn-int-ext</td>
<td>0.06 ± 0.03</td>
<td>0.27 ± 0.05</td>
<td>0.7 ± 0.1</td>
</tr>
<tr>
<td>mMn-int-ext</td>
<td>0.08 ± 0.03</td>
<td>0.08 ± 0.01</td>
<td>0.83 ± 0.13</td>
</tr>
<tr>
<td>sed-ext</td>
<td>0.05 ± 0.02</td>
<td>0.014 ± 0.003</td>
<td>0.9 ± 0.1</td>
</tr>
<tr>
<td>hMn-int-in</td>
<td>0.13 ± 0.04</td>
<td>0.24 ± 0.04</td>
<td>0.6 ± 0.1</td>
</tr>
<tr>
<td>sed-in</td>
<td>0.31 ± 0.09</td>
<td>0.07 ± 0.01</td>
<td>0.56 ± 0.10</td>
</tr>
<tr>
<td>mMn-int-in</td>
<td>0.09 ± 0.03</td>
<td>0.18 ± 0.04</td>
<td>0.71 ± 0.12</td>
</tr>
<tr>
<td>TrewV2.1s1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>hSr</td>
<td>0.83 ± 0.16</td>
<td>0.013 ± 0.003</td>
<td>0.09 ± 0.02</td>
</tr>
<tr>
<td>TrewR1.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>hCa-bone</td>
<td>0.96 ± 0.16</td>
<td>0.008 ± 0.002</td>
<td>0.021 ± 0.004</td>
</tr>
<tr>
<td>hMn-canal</td>
<td>0.29 ± 0.09</td>
<td>0.07 ± 0.01</td>
<td>0.63 ± 0.11</td>
</tr>
<tr>
<td>hSr</td>
<td>0.61 ± 0.12</td>
<td>0.016 ± 0.003</td>
<td>0.11 ± 0.02</td>
</tr>
<tr>
<td>TrewR6.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>hCa-bone</td>
<td>0.91 ± 0.17</td>
<td>0.007 ± 0.001</td>
<td>0.077 ± 0.016</td>
</tr>
<tr>
<td>lCa-canal</td>
<td>0.20 ± 0.07</td>
<td>0.005 ± 0.001</td>
<td>0.78 ± 0.13</td>
</tr>
<tr>
<td>HaV2.1s1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>hCa-bone</td>
<td>0.72 ± 0.13</td>
<td>0.006 ± 0.001</td>
<td>0.031 ± 0.006</td>
</tr>
<tr>
<td>hCa-sed</td>
<td>0.68 ± 0.13</td>
<td>0.025 ± 0.005</td>
<td>0.080 ± 0.016</td>
</tr>
<tr>
<td>hFe-int</td>
<td>0.28 ± 0.08</td>
<td>0.049 ± 0.010</td>
<td>0.63 ± 0.11</td>
</tr>
<tr>
<td>hSr-bone</td>
<td>0.95 ± 0.16</td>
<td>0.0057 ± 0.0011</td>
<td>0.027 ± 0.005</td>
</tr>
<tr>
<td>HaTn1.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ext-sed</td>
<td>0.19 ± 0.07</td>
<td>0.012 ± 0.004</td>
<td>0.66 ± 0.12</td>
</tr>
<tr>
<td>ext-sed</td>
<td>0.07 ± 0.03</td>
<td>0.85 ± 0.15</td>
<td>0.024 ± 0.005</td>
</tr>
<tr>
<td>tendon</td>
<td>0.96 ± 0.17</td>
<td>0.0042 ± 0.0009</td>
<td>0.024 ± 0.005</td>
</tr>
<tr>
<td>in-sed</td>
<td>0.84 ± 0.17</td>
<td>~ 0.002</td>
<td>0.057 ± 0.012</td>
</tr>
<tr>
<td>HaR1.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>bone</td>
<td>0.95 ± 0.17</td>
<td>0.006 ± 0.001</td>
<td>0.030 ± 0.006</td>
</tr>
<tr>
<td>in-sed</td>
<td>0.92 ± 0.17</td>
<td>0.006 ± 0.001</td>
<td>0.031 ± 0.006</td>
</tr>
</tbody>
</table>

Table 3.2: Determined concentrations of key elements for samples. Only elements in the range of $Z = 20$ to $Z = 39$ are considered.

determined concentrations for the sediments are given in fig. 3.27. The map is divided, as shown previously in fig. 3.14, into the parts interior and exterior to the bone, then further divided into the sediment-bone interface and sediments exterior to that. The $C_{Fe}/C_{Mn}$ ratio is the same for the highest Mn ($Z = 25$) regions inside and outside of the bone, suggesting it is the same mineral. That this is the case becomes even more evident with the determined values of this ratio given in table 3.4. It is likely that the high Mn content of the interface is due to varying amounts of this mineral, suggested by the data in table 3.4 to be of the form $(Fe_5Mn_2)X$, for some anion $X$. The more general trends of these elements are shown in fig 3.27.
Table 3.3: Determined concentrations of key elements for samples. Only elements in the range of $Z = 20$ to $Z = 39$ are considered.

<table>
<thead>
<tr>
<th>Sample - Region</th>
<th>$C_{Cu}$</th>
<th>$C_{Zn}$</th>
<th>$C_{Sr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>hMn-int-ext</td>
<td>$\sim 7 \times 10^{-5}$</td>
<td>$\sim 1 \times 10^{-4}$</td>
<td>0.0030 ± 0.0007</td>
</tr>
<tr>
<td>mMn-int-ext</td>
<td>$\sim 1 \times 10^{-4}$</td>
<td>$\sim 2 \times 10^{-4}$</td>
<td>0.0031 ± 0.0007</td>
</tr>
<tr>
<td>sed-ext</td>
<td>$\sim 8 \times 10^{-5}$</td>
<td>$\sim 3 \times 10^{-4}$</td>
<td>0.0030 ± 0.0008</td>
</tr>
<tr>
<td>hMn-int-in</td>
<td>$\sim 3 \times 10^{-5}$</td>
<td>$\sim 7 \times 10^{-5}$</td>
<td>0.0035 ± 0.0004</td>
</tr>
<tr>
<td>sed-in</td>
<td>$\sim 2 \times 10^{-5}$</td>
<td>$\sim 9 \times 10^{-5}$</td>
<td>0.0047 ± 0.0007</td>
</tr>
<tr>
<td>mMn-int-in</td>
<td>$\sim 3 \times 10^{-5}$</td>
<td>$\sim 8 \times 10^{-5}$</td>
<td>0.0035 ± 0.0007</td>
</tr>
<tr>
<td>hSr</td>
<td>$\sim 8 \times 10^{-5}$</td>
<td>$\sim 1 \times 10^{-4}$</td>
<td>0.049 ± 0.006</td>
</tr>
<tr>
<td>hMn-canal</td>
<td>$\sim 1.5 \times 10^{-4}$</td>
<td>$\sim 1.0 \times 10^{-4}$</td>
<td>0.0015 ± 0.0003</td>
</tr>
<tr>
<td>hSr</td>
<td>$\sim 2 \times 10^{-5}$</td>
<td>-</td>
<td>0.0018 ± 0.0004</td>
</tr>
<tr>
<td>Ca-bone</td>
<td>$\sim 4 \times 10^{-6}$</td>
<td>$\sim 1.1 \times 10^{-4}$</td>
<td>0.0022 ± 0.0003</td>
</tr>
<tr>
<td>Ca-canal</td>
<td>$\sim 1 \times 10^{-6}$</td>
<td>$\sim 5 \times 10^{-5}$</td>
<td>0.0032 ± 0.0006</td>
</tr>
<tr>
<td>hSr-bone</td>
<td>$\sim 3.6 \times 10^{-5}$</td>
<td>-</td>
<td>0.007 ± 0.001</td>
</tr>
<tr>
<td>hFe-int</td>
<td>$\sim 3 \times 10^{-5}$</td>
<td>$\sim 6 \times 10^{-4}$</td>
<td>0.0010 ± 0.0002</td>
</tr>
<tr>
<td>hSr-bone</td>
<td>$\sim 6 \times 10^{-4}$</td>
<td>-</td>
<td>0.0021 ± 0.0004</td>
</tr>
<tr>
<td>tendon</td>
<td>$\sim 6 \times 10^{-4}$</td>
<td>$\sim 2 \times 10^{-3}$</td>
<td>0.011 ± 0.001</td>
</tr>
<tr>
<td>bone</td>
<td>$\sim 3 \times 10^{-5}$</td>
<td>$\sim 2 \times 10^{-4}$</td>
<td>0.008 ± 0.001</td>
</tr>
<tr>
<td>in-sed</td>
<td>$\sim 3 \times 10^{-5}$</td>
<td>$\sim 2 \times 10^{-4}$</td>
<td>0.008 ± 0.001</td>
</tr>
</tbody>
</table>

The lowest Mn concentrations are found in the sediments exterior to the bone and bone-sediment interface. The elevated Mn in the bulk interior sediment with respect to the bulk exterior sediment may suggest locally concentrated bacterial activity or favourable precipitation conditions. It is also apparent that the interior sediments alone contain As ($Z = 33$) and Y ($Z = 39$). The exterior also shows elevated Cu ($Z = 29$) and Zn ($Z = 30$), but a similar ratio of the two when compared to the interior sediments. These observations suggest some degree of segregation between the bone's interior and exterior, despite their many similarities in composition.

The *T. rex* rib samples give an indication of the chemistry inside of the bone
Table 3.4: $C_{Fe}/C_{Mn}$ ratio for different regions of the TrexV2.1s0 sample, in particular, inside and outside of the bone. There is strong agreement between the high Mn concentration regions of the interface. This is suggested to represent the purest example of the Mn mineral that is present in the interface region. Appended is the $C_{Fe}/C_{Mn}$ for the highest Mn region of the interface of TrexV2.1s1. It agrees with what is seen for TrexV2.1s0.

samples, where fractures have not allowed sediments, but only interstitial fluids to enter. Concentrations for regions indicative of these samples are in fig. 3.28. The high Mn ($Z = 25$) and low Ca ($Z = 20$) regions represent the Harvesian canals of TrexR1.1 and TrexR6.1, respectively. The high Ca regions represent the bone surrounding the canals. There is a general similitude between the canals and likewise for the bones. The trends of the bone and canal are similar in TrexR6.1 for Cu ($Z = 29$) and Zn ($Z = 30$). The bone shows elevated Cu and Zn, but the ratio of the two is similar to the sediment of the same sample. Elevated Zn is also found in TrexR1.1. The Zn concentration of both bones agree, as do the As concentrations. The proportions of Zn and As in these bones is highly different from what is seen in the bone infill.
This is could be suggestive of a biological origin. Elevated Zn was observed in fossil bones in [3], where it was suggested to be indicative of the original fossil chemistry. However, As has previously (M.B. Goodwin et al., 2007) been seen to be incorporated into fossils through other sources. Both elements may be in the bone in proportion to Ca, but for different reasons, one related to original composition, the other to the potential for As absorption in the fossil. The Sr and Y concentrations seem more closely related to the particular sample, than to their sub-regions. The $C_{Sr}/C_{Y}$ ratio is more similar between the bone and sediment of one sample, than between the bones or between sediments of different samples. Due to the small size of the canals, it could be that the Sr and Y emissions from the sediments have been contaminated by emissions from the surrounding bone.

Figure 3.28: Determined element fractions for TrexR1.1 and TrexR6.1. (a): $Z = 20$ to $Z = 26$. (b): $Z = 27$ to $Z = 40$. (Original In Colour)

The question of the source of the elements for the formation of the mineral infilling the canals can be better addressed by looking at the supported concentrations of S ($Z = 16$), Fe ($Z = 26$) and their relation to one another. As noted earlier, there is S present in the canals, suggesting the presence of pyrite or similar minerals, which are commonly associated to bacterial processes, when sufficient S is present [15], [16]. For the sample TrexR1.1, one has that $C_{Fe} = 0.16 \pm 0.03$ and $C_{S} \sim 0.65$, implying $C_{S}/C_{Fe} \sim 4$. On the other hand, for the sample TrexR6.1 one finds that
\[ C_{Fe} = 0.27 \pm 0.05 \text{ and } C_S \sim 0.60, \text{ implying } \frac{C_S}{C_{Fe}} \sim 2.2. \] The latter value is very close to that of pyrite \((FeS_2)\), with a nominal value of \(\frac{C_S}{C_{Fe}} = 2\). The former may be consistent with pyrite, but a high uncertainty in \(C_S\) limits what can be drawn from this value. The sulphur K\(\alpha\) peak is at the lower end of the detectable emissions at VESPERS, and, although its presence is known, there is a large uncertainty in related concentration determinations. It is for this reason that approximate values are quoted. In either case, the result is consistent with minerals resulting from the actions of bacteria during the original decay of the specimen. This added support for the presence of sulphur compounds in and around the sample suggest that it is indeed a variation of baryte or celestite that is present in the high Sr regions of the samples, as opposed to a carbonate mineral like strontianite \((SrCO_3\) from \([47]\)). Of course, the depositional setting is known to have been carbonate rich; therefore, carbonate compounds cannot be completely ruled out. The segregation of the mineral infill (pyrite) of the TrexR1.1 sample and the high Sr mineral suggest different times of deposition. The prevailing pore fluids may, therefore, not have been rich in S at the time of deposition of this mineral.

The Frenchman hadrosaur shows both similarities to and differences from the *T. rex*. The concentrations, depicted in fig. 3.29 show that the sediment-bone interface forms a unique region. The bone and sediments are again distinguishable, even in spite of the cement being Ca-rich \((Z = 20)\) in this instance. This is made especially clear by the Sr \((Z = 38)\) and Y \((Z = 39)\) concentrations. Their elevation and unique ratio in the bone may be suggestive of dietary intake, or other biological origin. It should be noted that the \(\frac{C_{Sr}}{C_Y}\) ratio in this hadrosaur bone, agrees with that in the bone (and canal infill) of the TrexR6.1 sample just discussed. Both show a value of \(\frac{C_{Sr}}{C_Y} \sim 1.5\). The interface is again high in Mn \((Z = 25)\) and Fe \((Z = 26)\), suggesting bacterial activity in this layer of the sediment.

The Wapiti Formation samples offer a considerable contrast to the Frenchman
samples, as can be seen in fig. 3.30. First to be considered is whether there is any similarity between the interior and exterior sediments. It can be seen that the two exterior sediment points (these are two single point data collected with an incident beam diameter of \( \leq 10 \) \( \mu \text{m} \), not averaged map regions) are highly different from the interior sediments. The trends of the two exterior points are similar, as are the interior’s to some extent. The bone and tendon also share similar trends.

The Cu (\( Z = 29 \)), Zn (\( Z = 30 \)) and Sr (\( Z = 38 \)) concentrations are also of interest. The \( C_{Cu}/C_{Zn} \) ratio is similar between the tendon and bone, likewise for the
interior and exterior sediments. The $C_{Sr}$ are also similar for these bone and tendon samples. The exterior sediments show considerable variation. There is a conspicuous similarity between the $C_{Sr}$ of one of the exterior sediment data (red squares in fig. 3.30) and the bones. However, looking at the concentrations relative to that of Ca in each sample, more definite trends appear, as seen in fig. 3.31. The $C_{Sr}/C_{Ca}$ ratio of the bone and tendon agree with one another. All sediments except the interior sediment of the tendon agree. The interior sediment of the tendon is still easily distinguished from the bone and tendon. The implication is that these subregions of the samples share similar sources for these elements. A biological source in the case of the bone and tendon. Other sources for the sediments. Nickle is only present in the sediments, suggesting a link between the interior and exterior sediments, in spite of their differences. Arsenic is confined to the exterior sediments.

![Figure 3.31: Determined relative element fractions for Wapiti samples. Concentrations are given relative to that of Ca in each sample. (Original In Colour)](image)

The interior sediments are poor in Mn ($Z = 25$), Fe ($Z = 26$) and S ($Z = 16$) when compared to the Frenchman samples. This suggests either replacement or a difference in the degree or form of bacterial action between the depositional settings. It is still likely that the mineral infilling the bone and tendon is a precipitate of the interstitial fluids that cemented the surrounding rock. The mineral is also largely composed of low-Z elements, which agrees with other analysis [29] that has suggested
a carbonate cement. The Frenchman deposits seem to imply a higher degree of bacterial activity, or activity of a different nature, when compared to the Wapiti deposits. This is in keeping with the conditions for exceptional preservation at the Wapiti Formation bone bed.

The high Sr ($Z = 38$) regions also share a degree of similarity between the hadrosaur and T. rex specimens from the Frenchman formation, as shown in fig. 3.32. The $C_Y$, $C_{Zn}$ and $C_{Mn}$ values differentiate them from the high Sr hadrosaur bone. It is likely this is a precipitate that does not represent the early Fe, S, Mn rich pore fluids, but a mineral due to a separate precipitation event. It is likely that the cracks in and on the sides of the bones, where these regions are found, provided a nucleation point for the mineral, precipitating it out of the water passing through the sediment and bone.

Figure 3.32: Determined element fractions for high Sr regions. The Hav2.1s1 region is average high Sr bone, to be contrasted with the high Sr pockets from the TrexV2.1 and TrexR1.1 samples. (a): $Z = 20$ to $Z = 26$. (b): $Z = 27$ to $Z = 40$. (Original In Colour)
Chapter 4

Summary

4.1 Conclusions

A variety of qualitative and quantitative analysis tools for synchrotron XRF analysis have been developed and applied to fossils from the Frenchman and Wapiti formations. Though assembled for the particular challenges and needs of this work, they are generally applicable. The tools shown here allow for the identification of unique mineral features in XRF maps, and for the quantitative determination of the element concentrations in those features. This has led to the characterization of several diagenetic effects in the samples considered.

A clear line can be drawn between the diagenetic conditions to which the Frenchman Formation tyrannosaur and Wapiti Formation hadrosaur were subjected. Evidence for the presence of the products of the bacterial breakdown of organic matter, in and around the tyrannosaur and hadrosaur fossils, has been given. However, the data suggest the exact nature and extent of that activity was different at the respective fossil sites.

It has also been shown that the effective beam method can be successfully applied to a variety of samples measured on the VESPERS beamline at the CLS. The
method appears to be accurate for the range of elements presented here. A few limiting scenarios were found. In particular, when few of the major sample constituents are detected, a decrease in the accuracy of determined concentrations for those major constituents can result. Some deviations for Rb and Sr were observed. The likely cause being the unaccounted for intrinsic detector efficiency. Having determined a functional form for the effective beam intensity as a function of atomic number, the method can be used for a wider range of elements. Element concentrations in agreement with nominal values were determined for several natural minerals, in addition to the reference sample, SRM 610, used to define the beam. It would be beneficial to measure major and trace element concentrations in these natural minerals via another method, such as laser ablation or another stoichiometric method. This will help to better evaluate the extent to which the effective beam method is accurate over a range of elements and element concentrations (ppm to major constituents).

4.2 Remarks

The research presented here provides a firm base for further analysis of fossil and mineral samples using sXRF. A large volume of data has been collected, and can be similarly analyzed to further determine diagenetic effects and find traces of original fossil chemistry. Further refinements are also possible for the effective beam method. In particular it can be tested for a wider range of element emissions including L-shell emissions, given appropriate standards. The influence of inhomogeneity of standards can also be assessed. By continuing to apply diverse analysis methods to well chosen fossil samples, there is a great potential for developing an ever deeper understanding of local diagenetic processes and with that, past ecosystems. The results shown here hint at many curiosities hidden in these fossils and their sediments, and have also shown that sXRF is an effective means to understanding them. The ability to analyze
the minute details of the diagenetic processes, and with each process a portion of the history of an animal and ecosystem, provides an opportunity that must be seized.

### 4.3 Other Contributions

My work for the Integrated Palaeontology Working Group has extended beyond what is presented above. Many hours were spent on several different beamlines at the Canadian Light Source, collecting data for this and other research in the group. Much effort was also spent preparing samples for these shifts. I also participated in three field work sessions to help with the sedimentological analysis of the Frenchman Formation, and to help acquire fossil samples for the Royal Saskatchewan Museum and this work. I have also set up and maintained the group’s website which is used for inter-group communication and outreach. I have also written the C++ based programs used for the analysis presented here and for other analysis in the Integrated Palaeontology Working Group.
Bibliography


[33] ImageJ, Java image processing


