Uranium(VI) uptake by geological materials, characterisation by luminescence spectroscopy

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Fig. 5-20: PLIM and lifetime distribution of uranyl(VI) bound to a 50:50 mixture of bayerite and silica gel at pH 6.09. Only the bayerite rich region is included in the model. The microscopy image (left) and associated lifetime distribution (right) are shown for both the first and second exponential terms (τ), for more detail consult Fig. 5-7 caption.

Fig. 5-21: PLIM and lifetime distribution of uranyl(VI) bound to a 50:50 mixture of bayerite and silica gel at pH 6.09. Only the silica rich central aggregate is included in the model. The microscopy image (left) and associated lifetime distribution (right) are shown for both the first and second exponential terms (τ), for more detail consult Fig. 5-7 caption.

Fig. 5-22: Raman microscopy image of the same sample as studied by PLIM of the sample mixture at pH 6. Characteristic mineral shifts for bayerite and silica gel have been used to colour the image, blue representing the bayerite Raman shift at 550 cm^{-1}, and red indicating the D_{1} Raman shift typically observed for silica gel. More detail is provided in the methods (section 2.5).

Fig. 5-23: PLIM and lifetime distribution of uranyl(VI) bound to a 50:50 mixture of bayerite and silica gel at pH 8.53. The microscopy image (left) and associated lifetime distribution (right) are shown for both the first and second exponential terms (τ), for more detail consult Fig. 5-7 caption.

Fig. 5-24: PLIM and lifetime distribution of uranyl(VI) bound to a 50:50 mixture of bayerite and silica gel at pH 9.69. The image is fit to a single exponential but uses slightly different binning and background parameter due to large differences in intensity. The microscopy image (left) and associated lifetime distribution (right) are shown for both the first exponential terms (τ), for more detail consult Fig. 5-7 caption.

Fig. 5-25: The lifetime distributions determined by PLIM of uranyl(VI) bound to a mixture of silica gel and bayerite (1:1 by weight) at pH 4, 6, 8 and 10. The x-axis is on a log_{10} scale to aid comparison, the y-scale is the number of pixels.

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Fig. 5-30: The lifetime distributions determined by PLIM of uranyl(VI) bound to montmorillonite at pH 4, 6, 8 and 10. x-axis is on a log scale to aid comparison.

Table 8-1: The complete parameter set for all low temperature lifetime measurements. Sample code is [(pH)(mineral)]. All values are quoted to 2 decimal places except the lifetime values (in ns) which are to 0 decimal places. If a measurement is missing, it’s because it was not possible to resolve a luminescence decay.

Fig. 8-1: XRD pattern of montmorillonite STx-1b

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Fig. 8-6: XRD pattern of kaolinite

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Fig. 8-11: Fluorescence intensity images for samples of bayerite, silica gel, montmorillonite and a mixture of silica gel and bayerite, loaded with uranyl(VI). Max intensity per pixel = 200.

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the mean plus or minus one standard deviation, to help illustrate the range of values. Columns and rows are grouped as indicated by the mineral and pH headers.

**Fig. 8-18:** Fluorescent lifetime maps for all loaded samples fitted to a single exponential decay. Distribution histograms have been fixed at 500 to 3000 ps. Any fit outside of the chi2 range 0.5 to 2.5, or below a threshold value, is excluded from the distribution histogram and appears in black or white in the FLIM image.

**Table 8-2:** Table of input parameters for fitting FLIM of blank samples. Offset is set manually and is an average value from photons collected between T8 and T11 (Each pixel is represented by 256 T windows, or bins, over 10 ns, i.e. T=2.3 ps. The laser pulse, i.e. the IRF is observed at approximately T14 to T19, a decay is measured from T19). *value rounded from a representative pixel.

**Table 8-3:** FLIM for loaded samples. FLIM for all samples are defined by a single incomplete exponential decay. *value rounded from a representative pixel.
### List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT</td>
<td>Density Functional theory</td>
</tr>
<tr>
<td>EDL</td>
<td>Electrical Double Layer</td>
</tr>
<tr>
<td>EXAFS</td>
<td>Extended X-ray Absorption Fine Structure</td>
</tr>
<tr>
<td>FLIM</td>
<td>Fluorescence Lifetime Image Mapping</td>
</tr>
<tr>
<td>GDF</td>
<td>Geological Disposal Facility</td>
</tr>
<tr>
<td>HEXS</td>
<td>High Energy X-ray Scattering</td>
</tr>
<tr>
<td>HLW</td>
<td>High Level Waste</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>IEP</td>
<td>Isoelectric Point</td>
</tr>
<tr>
<td>ILW</td>
<td>Intermediate Level Waste</td>
</tr>
<tr>
<td>IR</td>
<td>Infra-Red, &gt;800 nm</td>
</tr>
<tr>
<td>LLW</td>
<td>Low Level Waste</td>
</tr>
<tr>
<td>LMCT</td>
<td>Ligand-to-Metal Charge Transfer</td>
</tr>
<tr>
<td>Log(K)</td>
<td>Complexation/formation constant</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>MM</td>
<td>Molecular Mechanics</td>
</tr>
<tr>
<td>MO</td>
<td>Molecular orbital</td>
</tr>
<tr>
<td>NEA</td>
<td>Nuclear Energy Agency</td>
</tr>
<tr>
<td>PARAFAC</td>
<td>Parallel Factor Analysis</td>
</tr>
<tr>
<td>PCA</td>
<td>Principle Component Analysis</td>
</tr>
<tr>
<td>PLIM</td>
<td>Phosphorescent Lifetime Image Mapping</td>
</tr>
<tr>
<td>PMT</td>
<td>Photomultiplier tube</td>
</tr>
<tr>
<td>PZC</td>
<td>Point of zero net charge</td>
</tr>
<tr>
<td>QM</td>
<td>Quantum mechanics</td>
</tr>
<tr>
<td>SCM</td>
<td>Surface Complexation Modelling</td>
</tr>
<tr>
<td>SHG</td>
<td>Second Harmonic Generation</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra-violet, &lt;400 nm</td>
</tr>
<tr>
<td>UO&lt;sub&gt;ax&lt;/sub&gt;</td>
<td>Uranium-Oxygen axial bond</td>
</tr>
<tr>
<td>UO&lt;sub&gt;eq&lt;/sub&gt;</td>
<td>Uranium-Oxygen equatorial bond</td>
</tr>
<tr>
<td>XAS</td>
<td>X-ray Absorption Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>XRF</td>
<td>X-ray Fluorescence</td>
</tr>
</tbody>
</table>
ABSTRACT

Mark Williams. Uranium(VI) Uptake by Geological Materials, Characterisation by Luminescence Spectroscopy. For the degree of Doctor of Philosophy from The University of Manchester, 2017.

Many of the wastes associated with the nuclear fuel cycle are toxic to the biosphere; advancing the use of high resolution spectroscopy applied to these materials will provide the chemical speciation of the interaction between nuclear waste and geological material, improving confidence in a permanent disposal method and informing clean-up operations. Luminescence spectroscopy of uranyl(VI) is a well-established technique for the molecular speciation of uranium-mineral interactions. This work explores the use of both micro- and macroscopic luminescence spectroscopy to expose uranyl(VI) speciative heterogeneity in a range of minerals which have been exposed to uranyl(VI) salt solutions. A comprehensive review of the available literature on the interaction of uranyl(VI) with a range of geological media is assessed and compared. The review finds considerable ambiguity in the speciation of uranyl(VI) at the mineral water interface. A database reporting the multi parametric luminescence properties of uranyl(VI) with silica gel, quartz, bayerite, boehmite, muscovite, kaolinite and montmorillonite (SWy-2 and STx-1b) is presented and discussed. Although some of the results are consistent with previously reported values, many newly identified species are reported and their identification speculated. Parallel factor analysis is used to deconvolute the excitation-emission matrix of uranyl(VI) sorbed to silica gel between pH 3 and pH 10. The results are used to identify the spectroscopic properties of complexes >\((\text{SiO})_2\text{UO}_2\) and >\((\text{SiO})_2\text{UO}_2\text{OH}\) and thus new complexation coefficients (log(K)) for their formation with the silica gel surface are determined, log(K_1) = 9.22 ± 0.02 and log(K_2) = 3.45 ± 0.01, respectively. The investigation also provides insight into the fundamental properties of uranyl(VI) excitation pathways, which are not yet fully understood. Confocal microscopy and phosphorescent lifetime image mapping (PLIM) is used to expose the sub-micron heterogeneity of uranyl(VI) sorption complexation across mineral surfaces of silica gel, bayerite and montmorillonite (STx-1b). The results suggest that changes in the uranyl(VI) lifetime can be used to observe and understand submicron changes in uranyl(VI) complexation at hitherto unknown temporal resolution.
DECLARATION

No portion of the work referred to in this thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.

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Thank you Elizabeth. You bring out the best in me and I don't think I could have completed this without you.
1 INTRODUCTION

1.1 Wider context and research overview.

One of the most pressing challenges facing society today is the management of existing and future waste forms arising from nuclear energy production.\(^1\) Although radioactivity occurs naturally in the environment, more than 60 years of anthropogenic activities including the mining, fabrication, operation and decommissioning of commercial nuclear energy production has led to the generation and concentration of radioactive material.\(^2\) Poorly managed legacy wastes present a requirement for the remediation of contaminated land.\(^3\) The impact such radioactive contamination poses to the wider ecosystem is intricately linked to the biological and geological availability of the radionuclide in question,\(^4,5\) which is dictated by their concentration and chemical form (speciation and oxidation state). Given that uranium comprises the majority of spent nuclear fuel by mass,\(^6\) the physical and chemical interaction of uranium with naturally occurring minerals has become an important strategy in managing safe disposal by preventing leaching, particularly in a Geological Disposal Facility (GDF), which is being considered around the world as the most pertinent form of nuclear waste disposal. Over the lifespan of the proposed GDF, one of the principle hazards is a change in the chemistry of uranium that results in it leaching from the repository, breaching the primary containment, entering the engineered environment, and eventually the biosphere.\(^7\)

Improving the understanding of the interaction of uranium with geological materials will inform the remediation of contaminated lands\(^8\) as well as the safety case for a GDF.\(^9,10\) However, these interactions are typically studied at the macroscopic level by techniques such as X-ray absorption spectroscopy (XAS). These measurements inherently observe the averaged chemical state, meaning that smaller contributions remain hidden or worse, invalidate the assignment of the observed averaged signal. The heterogeneous nature of the interactions between uranium and minerals can only realistically be achieved provided that the speciation and geochemistry can be more completely understood \textit{in situ} on a microscopic level, to enable the accurate modelling of radionuclide transport. The primary aim of this work is to contribute to the understanding of the molecular level interactions between uranium and minerals using luminescence spectroscopy and
microscopy, in order to better inform the modelling of the environments relevant to both the remediation of contaminated land and the engineered barrier of a GDF.

The most relevant form of uranium in these environments is uranium in the +6 oxidation state. Under an oxic environment, uranium will predominate in its fully oxidised form uranyl(VI), UO$_2^{2+}$. Uranyl(VI) is highly photoluminescent (herein referred to as luminescent) under ultraviolet light: its characteristic excitation and emission spectra (Fig. 1-1) are used to detect uranium$^{11,12}$ at the concentrations typically found at contaminated sites,$^{13}$ or anticipated in the later stages of a GDF (i.e. upon contact of waste with backfill material). By recording and analysing the various properties of uranyl(VI) luminescence (i.e. the excitation, emission, and lifetime properties) the speciation can be determined.$^{14}$

![Excitation and Emission Spectra](image)

**Fig. 1-1:** A representative excitation and emission spectrum of uranyl(VI) recorded at 77K. Note the excitation takes place in the ultraviolet (<400 nm) and violet (400 - 450 nm) regions of the electromagnetic spectrum while the emission from uranyl(VI) is green (~520 nm).

Owed in part to its low cost and practicality, luminescence appears frequently in the current literature. However, research groups adopt varied approaches to experimentation, making comparison between published data very difficult.$^{15}$ Luminescence lifetimes are particularly sensitive to experiment temperature and uranyl(VI) concentration. In addition, emission spectra of aqueous uranyl(VI) and uranyl(VI) mineral interactions are often complex with several overlapping spectral features, which can complicate data analysis. Therefore, luminescence data may be considered only qualitative, or supplementary to other spectroscopies. This work aims
to address some of the issues often encountered when determining the speciation of uranyl(VI) interactions with mineral systems. This includes the interaction of uranium with silica gel, quartz, bayerite, boehmite, montmorillonite (STx-1b and SWy-2), muscovite and kaolinite (KGa).

To achieve this, a comprehensive theoretical introduction to the spectroscopy used is described (Section 1.2 and 0). The wider literature describing the water-mineral interface is summarised (Section 1.4) and placed into the wider context of the speciation of uranyl(VI) interactions at this interface (Section 1.5 and 1.6). A justification and explanation for the experimental approach taken is provided (chapter 2) before reporting the excitation, emission and lifetime properties for uranyl(VI) sorbed to the full range of minerals considered, under well controlled conditions (chapter 3). Speciation is then determined for uranyl(VI) sorbed to the single mineral silica gel ($\text{SiO}_2$) by the analysis of excitation-emission matrices through the use of parallel factor analysis (PARAFAC)\(^{16}\) (chapter 4). Luminescence lifetime microscopy of uranyl(VI) sorbed to silica gel, bayerite ($\alpha$-$\text{Al(OH)}_3$) and montmorillonite (STx-1b) using state-of-the-art phosphorescent lifetime image mapping (PLIM) is assessed (chapter 5). The three results chapters serve to demonstrate the depth of information contained within the luminescence of uranyl(VI) and provides comprehensive ways for exposing this detail by introducing advanced PARAFAC analysis and lifetime microscopy to this field of research.

### 1.2 Uranium in the environment

Uranium is chemotoxic and radioactive and is therefore a hazard if concentrated in the biosphere. Uranium may phytoaccumulate\(^{17}\) and if ingested, can cause complications in the functioning of the kidney, brain, liver and heart as it is a potent nephrotoxin.\(^{18}\) All isotopes of uranium are unstable. Comprising 99.27% of uranium in the Earth’s crust, $^{238}\text{U}$ is the most abundant uranium isotope and has a half-life of $4.468 \times 10^9$ years (Table 1-1) and its decay chain contains nine elements eventually ending in $^{206}\text{Pb}$. Because of its long half-life and thus low specific radioactivity, uranium’s chemical toxicity is considered to be a far greater risk to life than its radioactivity, by at least two orders of magnitude.\(^{19}\)
Table 1-1: the natural abundance of the three most common uranium isotopes and their associated radioactivity

<table>
<thead>
<tr>
<th>Uranium isotope</th>
<th>Fraction (%)</th>
<th>Half life (y)</th>
<th>Activity (Bq/Kg U_{nat})</th>
</tr>
</thead>
<tbody>
<tr>
<td>238</td>
<td>99.2742</td>
<td>4.468(3)×10⁹</td>
<td>1.27 x 10⁷</td>
</tr>
<tr>
<td>235</td>
<td>0.7204</td>
<td>7.04(1)×10⁸</td>
<td>5.7 x 10⁵</td>
</tr>
<tr>
<td>234</td>
<td>0.0054</td>
<td>2.455(6)×10⁵</td>
<td>1.2 x 10⁷</td>
</tr>
</tbody>
</table>

The nuclear fuel cycle has resulted in elevated concentrations of uranium in the environment. For example, in Colorado at the United States Department of Energy Rifle site, elevated levels (e.g. up to 50 times more uranium than is typical)²⁰ of uranium have been detected in groundwater leached from the former ore processing facility.¹⁹ Such environmental contamination presents an uncontrolled source of radiation. Investment into the scientific understanding of the interactions of uranium with the environment, especially at the molecular level, will reduce any eventual costs in the event contaminated land is remediated.²¹ Such advancements will also add important understanding to the mitigation of risks associated with the disposal of intermediate and high level wastes in a GDF scenario.²²

The operation and decommissioning of nuclear power plants generates the vast majority of radioactive waste. The first commercial nuclear power plant was opened in 1956, Calder Hall in West Cumbria, UK. Today, at least 449 commercial nuclear reactors are in operation, providing 11% of the world’s energy needs, but also producing 12,000 tonnes of high level waste (HLW) each year.²³–²⁵ About 94% of the UK’s nuclear waste is classified as low level or very low level waste, most of which is a result of facility dismantling and the waste is already disposed of at the Low Level Waste (LLW) repository in Drigg.¹ About 6% of the remaining waste is intermediate and 0.01% is high level waste. The waste itself is predominantly formed of ‘unburnt’ uranium (93.4%), fission products (5.15%), plutonium (1.27%) and other transuranic elements (0.14%).⁶

In the UK, the waste is separated by the PUREX (Plutonium Uranium Refinement by Extraction or Plutonium Uranium Redox Extraction) process. This process takes

¹ However, the site is nearing capacity and has undergone significant restructuring such as a new waste hierarchy. This has resulted in much of the wastes originally sent to Drigg being redirected (85% in 2014) towards ‘alternative disposal routes’, such as commercial landfill.¹⁹
advantage of the different redox properties of uranium and plutonium to separate the uranium and plutonium in spent fuel from the fission products and other transuranic waste products for re-use in MOX reactors (UK) or for interim storage pending long term disposal. Current reprocessing plants are due to close in 2018, without fuel reprocessing the UK will eventually transition to an open fuel cycle (i.e. no fuel reprocessing/recycling) at which point current and future used fuel will all become projected for final disposal around 2075, via a GDF. A closed fuel cycle is arguably more ecologically responsible (it theoretically requires less mining of raw materials i.e. uranium), research at NNL (National Nuclear Labs) is currently on-going into more advanced recycling and reprocessing options for spent nuclear fuels.

![Fig. 1-2](image)

**Host geology**
- sedimentary
- crystalline

**Backfill material**
- Clay (impermeable)
- Cement (alkaline)

**Container**
- Steel canister
- Copper canister

**Wasteform**
- HLW Borosilicate glass
- ILW Cement

*Fig. 1-2: A graphical representation of the multi-barrier concept. Alongside each barrier are examples of the most popular materials under consideration*

The purpose of a GDF is to reduce the hazard of nuclear wastes by making them irrecoverable, and to minimise the chance of remobilisation. Despite many proposals for a GDF around the world, the majority have yet to meet social and political consensus (i.e. the UK has so far not been successful in agreeing at a local as well as national level on a specified site for a GDF), However, Finland have approved a site, Olkiluoto, which is scheduled to begin construction in 2020. Despite this, the scientific aspects of a GDF are relatively well defined; a GDF will consist of multiple engineered barriers (see Fig. 1-2). The first of these barriers is the waste form itself, which is typically vitrified (for HLW), or encapsulated into a cement/ceramic (for intermediate level waste). Second is
the container, typically a titanium-rich steel, but potentially copper (proposed in the Swedish/Finnish design). Most steel canisters are expected to fail after several thousands of years, meaning that a large amount of research has gone into the repositories backfill material. This barrier would either be cement, salt or clay. The combination of a copper canister and stable clay buffer, i.e. bentonite, has received considerable research and is currently considered to be the most effective backfill material for HLW. This third barrier depends on many, often significantly interlinked, properties including that of the host geology. The final barrier is the host rock itself, which will be at least 200 m below ground level.

Despite no fixed site for a GDF, the UK is exploring the prospect of a combined cement and clay-based backfill scenario. The facility will contain two modules separated by the host rock by at least 500 m, one module will hold HLW and backfilled using clay and the second module will contain ILW and be backfilled with cement. Cement is advantageous due to its high pH which results in favourably reducing redox conditions. However, cement is more susceptible to fissures, which are to be expected over long geological time periods. Clays are favoured for their high plasticity (fissures are extremely unlikely), high sorption capacities and low hydraulic conductivity. However, they do not create the same favourable redox conditions as cements, depending instead on the formation of immobile surface complexes and slowing the intrusion of water.

Regardless of the final design, the modelling of any potential waste facility over the geological time periods required for the radioactivity to reduce to safe levels (of at least a million years) will require a thorough understanding of the possible interactions with the various engineered barriers. The host geology and backfill material will contain a mixture of minerals, most likely rich in aluminosilicate clays, which is the focus of this work.

1.2.1 Chemistry of uranium

Due to its redox chemistry in the natural and engineered environment, uranium can be fixed in a solid phase as U(IV) or in a solvated phase, as U(VI). Other oxidation states

\footnote{This results in rich uranium deposits at redox fronts, for example in a sandstone roll-front deposit like that at Powder River Basin, Wyoming, USA. See reference 199}
of uranium exist in near negligible quantities in the environment but are frequently isolated in high yield under laboratory conditions and range from +2 to +6.\textsuperscript{30} Uranyl(V) is of particular interest for its proposed involvement in the two-step one electron reduction pathway of U(VI) to U(IV).\textsuperscript{31}

The uranyl(VI) ion is a linear triatomic molecule, U(VI) is centred between two axial oxygen atoms (these bonds are herein referred to as UO\textsubscript{ax}) giving it an overall +2 charge. Electron donor atoms align along the equatorial plane to stabilise the positive charge of the uranium (for oxygen atoms, these bonds are referred to as UO\textsubscript{eq}). The hydrated uranyl(VI) ion contains a hydration shell of 4 to 6 equatorial water molecules. This hydrated uranyl(VI) ion is generally dominant in solution below pH 4, as the pH increases, hydrolysis occurs. In natural oxic water (pH range 4.5 – 9) uranyl(VI) is usually at least partially hydrolysed, as shown by the pH dependent equilibrium equations (1 and 2:

\[
[\text{UO}_2(H_2O)_4]^{2+} \leftrightharpoons [\text{UO}_2(H_2O)_3(OH)]^+ + H^+ \quad (1)
\]

\[
[\text{UO}_2(H_2O)_3(OH)]^+ \leftrightharpoons [\text{UO}_2(H_2O)_2(OH)_2] + H^+ \quad (2)
\]

When carbon dioxide is present in the atmosphere, it will undergo favourable carbonation dissolution with water to form carbonic acid via the dynamic equilibrium (equation (3)):

\[
\text{CO}_2 + H_2O \leftrightharpoons H_2\text{CO}_3 \quad (3)
\]

The carbonic acid then undergoes two successive reduction reactions with OH\textsuperscript{-} ions to produce a carbonate ion and two water molecules (equations (4) and (5)).

\[
\text{H}_2\text{CO}_3 + \text{OH}^- \leftrightharpoons \text{HCO}_3^- + \text{H}_2O \quad (4)
\]

\[
\text{HCO}_3^- + \text{OH}^- \leftrightharpoons \text{CO}_3^{2-} + \text{H}_2O \quad (5)
\]

The presence of carbonate (CO\textsubscript{3})\textsuperscript{2-} in a uranyl(VI) containing solution changes the chemistry of the uranyl(VI) cation significantly. Carbonate binds favourably to the uranyl(VI) cation, displacing water and lowering its overall charge and reducing its uptake properties towards clay minerals. The bonding of carbonate is largely controlled by the pH and Eh of the system. In general, a more alkaline pH (approx. pH >8) results in further reduction of carbonic acid and a greater presence of uranyl(VI)-carbonate
species, up to a maximum of 3 equatorial carbonate molecules. Conversely a more acidic solution (approx. pH 3) will contain negligible carbonate, when combined with the reduced likelihood of hydrolysis, the free uranyl(VI) ion, \{UO₂(H₂O)₅\}²⁺ is generally the most dominant species.²

1.2.2 Surface complexation of uranyl(VI)

The inner-sphere interaction of uranyl(VI) with minerals is via the amphoteric oxides that form at the surface of a mineral. Throughout this thesis various forms of oxide will be referred to but all can be generalised to the same ionisation and complexation principles which are outlined briefly here, in equation (6) and (7), where >XOH₂⁺, >XOH and >XO⁻ represent positively charged, neutral and negatively charged surface hydroxyl groups respectively:¹ Thus the nature of the surface will depend on the pH.

\[
>\text{XOH}_2^+ \rightleftharpoons >\text{XOH} + \text{H}^+ \quad (6)
\]

\[
>\text{XOH} \rightleftharpoons >\text{XO}^- + \text{H}^+ \quad (7)
\]

A cation such as uranyl(VI) will have a considerably greater chemical and cumblic attraction to the anionic >XO⁻ surface than the >XOH or >XOH₂⁺. Indeed, such valance bond theory considerations can often provide some insight into bonding,³² but usually only act as a basis for more complete considerations via surface complexation modelling, which considers the mineral morphology, a surface description (e.g. Stern layer), the pKₐ for all surface sites (most commonly determined via potentiometric titration) and then refined by spectroscopic data (i.e. luminescence).³³ Other methods such as molecular dynamics (based on experimentally derived constants)³⁴ or quantum mechanics (restricted electronic solution to the Schrödinger equation)³⁵ are computational based methods which also aim to describe the surface speciation.

Formation constants²² are the primary outcome of experimental work, for the improved simulation of environmental processes such as those in a GDF scenario or contaminated

¹ Throughout this work ‘>’ within a chemical formula is used to represent bonding to the bulk media
² K or β are used interchangeably in the literature to represent the formation constant within surface complexation modelling. Not to be confused with K_D (mL/g), which refers to the linear coefficient, often obtained from linear isotherms and interchangeably referred to as the partition coefficient or distribution coefficient. K_D is not applicable to a change in conditions such as metal concentration or salinity. A criticism of the formation constant (K, β) used in surface complexation models is that they assume aqueous chemistry somewhat correlates with adsorption. See reference ²²⁰ for more details.
land. Two generalised cases are shown in equations (8) and (9) where \( M^+ \) is a metal cation, such as \( \text{Na}^+ \) and \( M^{2+} \) is a divalent cation such as \( \text{UO}_2^{2+} \).

\[
> \text{XOH} + M^+ \rightleftharpoons > \text{XOM} + H^+
\]

\[
> \text{XOH} + M^{2+} + H_2O \rightleftharpoons > \text{XOMOH} + H^+
\]

Each process can be defined by the formation constant, \( K \), defined by equations (10) and (11), where curly brackets denote activity and square brackets denote concentration. These concepts are discussed in more detail and with greater relevance to uranium complexation in chapter 4.

\[
K_{>\text{XOM}} = \frac{[> \text{XOM}][H^+]}{[> \text{XOH}][M^+]} \quad (10)
\]

\[
K_{>\text{XOMOH}} = \frac{[> \text{XOMOH}][H^+]}{[> \text{XOH}][M^{2+}]} \quad (11)
\]
1.3 Luminescence

Luminescence is the electronic excitation and subsequent de-excitation of an electron, which is associated with the absorption and subsequent emission of a photon with a very specific, discrete quantum of energy. Generally, the emitted light is invariably of lower energy than the excitation light (this change is referred to as a Stokes shift) for a one-photon process, due to the vibrational relaxation (which is fast, \( \sim 10^{-12} \text{ s} \), see Table 1-2) in the excited state prior to emission, and/or the emission to an excited vibrational state (see Fig. 1-3, note the blue lines, representing excitation, are longer than the green lines, representing emission). Luminescence is subdivided into fluorescence and phosphorescence. The luminescence of uranyl(VI) is formally a phosphorescent process, meaning the absorption and emission requires an intermediary transition from an excited singlet state to an excited triplet state, such a transition is known as intersystem crossing (ISC). This process is inherently slow (the transition is forbidden due to the spin selection rule i.e. \( \Delta m_s = 0 \)), meaning that uranyl(VI) phosphorescence can persist from \( \mu \text{s} \) to \( ms \) after the excitation source is removed. Conversely, fluorescence does not involve ISC and emission is directly from the singlet excited state. The observed excitation and emission profiles are composed of several electronic excitation and emission transitions. The likelihood and thus observed intensity of each transition is determined by the various selection rules and molecular orbitals involved. In the case of the early actinides oxo ions, as with uranyl(VI), considerable complexity is introduced by the involvement of several molecular orbitals and how they are influenced by bonding with donor atoms in the equatorial plane.
Fig. 1-3: A Jablonski diagram of the phosphorescence process using the anharmonic oscillator. Light is absorbed and an electron is excited (blue lines) from the ground state \((S_0, v_0, v_1)\) to the first electronic excited state \((S_1, v_0\) to \(v_{12}\) in the case of uranyl(VI)). Vibrational relaxation to the vibrational ground state \((v_0)\) occurs rapidly. The excited singlet \((S_1, v_0)\) transfers to an excited triplet \((T_1, v_3)\) and is followed by vibrational relaxation \((T_1, v_0)\). Emission occurs from the excited triplet \((T_1, v_0)\) to the ground state \((S_0, v_0\) to \(v_6)\).

Table 1-2: A list of some common processes relevant to luminescence and the time taken at room temperature. \(S\) for a singlet electronic state and \(T\) for a triplet electronic state. Values taken from reference 36.

<table>
<thead>
<tr>
<th>Process</th>
<th>Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption</td>
<td>(10^{-15})</td>
</tr>
<tr>
<td>Vibrational relaxation</td>
<td>(10^{-13} - 10^{-12})</td>
</tr>
<tr>
<td>Internal conversion (IC)</td>
<td>(10^{-12} - 10^{-6})</td>
</tr>
<tr>
<td>Intersystem crossing (ISC) (S \rightarrow T)</td>
<td>(10^{-9} - 10^{-6})</td>
</tr>
<tr>
<td>Intersystem crossing (ISC) (T \rightarrow S)</td>
<td>(10^{-9} - 10^{-1})</td>
</tr>
<tr>
<td>Fluorescence</td>
<td>(10^{-9} - 10^{-7})</td>
</tr>
<tr>
<td>Phosphorescence</td>
<td>(10^{-6} - 10^{1})</td>
</tr>
</tbody>
</table>
1.3.1 Uranyl(VI) electronic structure

Despite its renowned optical properties and history, the electronic transitions which result in uranium’s green fluorescence were not widely accepted until collated and defined by the seminal work of Denning. The combination of atomic orbitals in uranyl(VI) are depicted in Fig. 1-4, and was largely determined from crystals of Cs₂UO₂Cl₄ and CsUO₂(NO₃)₃, measured at 5 K. The six highest occupied molecular orbitals (HOMOs), σₕ, σₜ, 2(πₙ), and 2(πₜ) are centred on the 2p orbitals of the oxygen atoms, meaning that the electron density is mostly associated with the oxygen atoms. These orbitals are bonding and thus suggest a formal bond order of three. These molecular orbitals (MOs) form due to mixing of the 5f and 6d orbitals of uranium with the 2p orbitals of oxygen, however the precise extent of overlap is somewhat unclear. For example, the MOs must also consider the 6p electrons, which are considered “pseudo-core”, because their XPS ionizations show large axial field splitting that correlate inversely with the U-O bond distance. In addition, the radial extension of the 6s uranium orbital is comparable to its 5f orbital, and must also be included in the formation of these HOMOs. Finally, the 2s oxygen orbital has near degeneracy to, and thus an interaction with the uranium 6p orbital, and is also included. This mixing is demonstrated in Fig. 1-4, which also includes the cubic set of orbitals for those involved. Highlighted in red are the atomic orbitals that mix to make the highest energy HOMO, the 6pz and 2pz. The lowest unoccupied molecular orbitals (LUMOs) of UO₂²⁺ are the 5fₕ and 5fΦ orbitals and are non-bonding as they are excluded by symmetry from the UOax bond, these orbitals have been highlighted in green in Fig. 1-4. The electronic excitation of uranyl(VI) is therefore formally a ligand-metal charge transfer transition involving excitation of an electron from a predominately 2p bonding orbital to a 5f non-bonding orbital. It is changes in the energetics of the HOMOs therefore, that influence the emission spectrum of uranyl(VI). In addition, the total symmetric (ν₁ Raman active) and asymmetric (ν₃ IR active) stretching frequencies of the UOax bond are indicative of the uranyl bond strength. These are observed between 700 to 870 cm⁻¹ (ν₁) and 800 to 1000 cm⁻¹ (ν₃) for fully hydrated uranyl(VI) with lower values indicating a weaker UOax bond and more electron donating equatorial ligands. This total symmetric
stretching vibration is observed as the vibrational fine structure super imposed on the emission spectrum of uranyl(VI).\footnote{Several recent reviews discuss these details, see references 30,44,183,201}

![Fig. 1-4: Uranyl(VI) molecular orbital diagram. Gerade orbitals are in red, ungerade orbitals in black. Crude point-drawn electron density plots are illustrated for the cubic set atomic orbitals using Orbital Viewer (software by David Manthey), the page plane matches the equatorial plane. HOMOs are highlighted in orange, LUMOs in green.}

1.3.2 Uranyl(VI) emission and excitation spectra

The steady state emission spectra of uranyl(VI) provide two key pieces of information about both the axial and equatorial bonding to the uranium atom. The first is the position of the highest energy peak, which is equal to the HOMO-LUMO energy gap. The second is the vibrational spacing between the first and second peaks, which provides the energy of the Raman active total symmetric stretching frequency ($\nu_1$). These two values combined indicate the bond strength of the UO$_6$ bond.\footnote{Due to the anharmonic oscillator (i.e. Morse potential), the spacing between the 2$^{nd}$ and 3$^{rd}$ peak and subsequent spacing will be smaller than the first, but this change is sometimes so minor, that the error associated with each peak maxima position is comparatively large. As such, some authors will report the average of the first few spacings.104} How these electronic transitions result in the observed spectra is depicted in Fig. 1-5.
Fig. 1-5: A Jablonski energy diagram depicting the excitation and emission of uranyl(VI). Three possible excitation routes are depicted, note that each results in the same emission. The solid purple arrow depicts excitation into a continuum of excited states (left) and the corresponding structureless character in the excitation spectrum at ~275 nm. The solid dark blue arrow depicts excitation into an excited singlet state of uncertain origin (left, see text for explanation of uncertainty) and the corresponding structured character in the excitation spectrum at ~370 nm (right). The solid light blue arrow depicts excitation into the first excited singlet state (left) and the corresponding structured character in the excitation spectrum. Three green arrows represent the emission from the excited triplet to the ground state (left) and the corresponding emission (right). Dotted arrows represent a radiationless transition (Kasha’s rule), which include but are not limited to a combination of internal conversion and vibrational relaxation. Red arrow represents intersystem crossing. Figure uses excitation and emission spectrum recorded at 77K, thus contributions from vibrational excited states are negligible. Figure redrawn and expanded from Drobot et al.¹⁴
Fig. 1-5 details some of the possible transitions leading to the emission of uranyl(VI). Each transition is shown only from the vibrational ground state, since most of the measurements in this thesis are carried out at liquid nitrogen temperatures (77 K), this increases the observed intensity by limiting quenching mechanisms but more importantly, it reduces the population of vibrational excited species. For example, when analysing the emission of uranyl(VI) at room temperature, it is necessary to identify the hot band emissions, which tend to overlap on the low energy side of the main peak emissions. To clarify this distinction, consider the vibrational energy population distribution. The population distribution of states is determined by the Boltzmann distribution (12)

\[
\frac{N_1}{N_0} = e^{-\frac{\Delta E}{k_B T}}
\]

where \(N_1\) is the population of the first vibrational excited state and \(N_0\) the population of the vibrational ground state, \(k_B\) is the Boltzmann’s constant and \(T\) is the temperature in Kelvin. In the case of a uranyl(VI) species with a typical vibrational energy difference (\(\Delta E\)) of \(\sim 800 \text{ cm}^{-1}\), \(N_1/N_0\) is 0.02 at room temperature (meaning that roughly 1 in every 50 molecules is vibrationally excited), and \(3 \times 10^{-7}\) at liquid nitrogen temperature (meaning only roughly 1 in 4 million molecules is vibrationally excited). It is therefore reasonable to assume near negligible vibrational excited hot band emissions for samples measured at 77K.

The electronic transitions resulting in a change in both electronic and vibrational energy (vibronic transition) occur too fast for a nuclear movement (i.e. internuclear separation is constant). The likelihood of a transition and thus the observed intensity, is determined by the overlap of the vibrational wave functions, which change as a function of internuclear separation (known as the Frank-Condon principle). For the excitation and emission in Fig. 1-5 the excitation transitions \(S_0\nu_0 \rightarrow S_1\nu_2\) and \(S_0\nu_0 \rightarrow S_x\nu_2\) are the most probable (thus we observe the greatest intensity at these energies). This likely suggests that \(x\) is 2, and that excitation in the \(\sim 370 \text{ nm}\) range is an excitation to a higher singlet state of uranyl(VI),\(^{38,40-42}\) the alternative is that this transition is a higher energy LMCT
from the donor atom bound in the equatorial plane to the empty 5f orbitals on uranium or to the excited state of a ligand.\textsuperscript{43,44}

These observations are useful for identifying significant change in the ligands bound to uranyl(VI) in the equatorial plane. For subtler changes in the ligand environment, such as the change in the rate of exchange of solvent molecules, the lifetime is considered more applicable.

### 1.3.3 Uranyl(VI) excitation-emission lifetime

The lifetime ($\tau$) of the excitation emission process can reveal more information about the electronic environment of the equatorial bonds than the excitation and emission spectra.

Following a pulse of excitation light, the total number of observed emissive photons (the recorded intensity) decreases exponentially as a function of time, the number of exponential components is generally consistent with (at least)\textsuperscript{1} the number of unique species in the illuminated sample. Therefore, lifetime data can be modelled to an exponential decay function. The models are characterised by the lifetimes of the exponential components, $\tau$, and the amplitudes of the exponential components, $a$ as a function of time, $t$.

\[
f(t) = e^{-\frac{t}{\tau}} \quad (13)
\]

\[
f(t) = a_1e^{-\frac{t}{\tau}} + a_2e^{-\frac{t}{\tau}} \quad (14)
\]

\[
f(t) = a_1e^{-\frac{t}{\tau}} + a_2e^{-\frac{t}{\tau}} + a_3e^{-\frac{t}{\tau}} \quad (15)
\]

Equation (13) is a single exponential model, adding a second or third exponential decay term provides the models for the double (14) and triple (15) exponentials, respectively. With the addition of terms comes the requirement for the acquisition of a greater

\textsuperscript{1} It’s possible that two or more unique species in a single sample may have near identical observed lifetimes, and will not be differentiated by lifetime measurement, thus the number of components indicates the minimum number of emissive species.
number of photons per time-resolved decay (e.g. a single exponential may require only 100s of photons, whereas a triple exponential will require many 1000s).\textsuperscript{45}

A shorter lifetime indicates an increase in the extent of non-radiative energy pathways. These non-radiative pathways are generally facilitated by quenchers. A quencher is a ligand, solvent molecule or foreign molecule that collides with and transfers energy from the excited triplet state of the uranyl(VI) molecule. The likelihood of energy transfer is proportional to the energetic overlap of the levels involved, (exactly like ISC in Fig. 1-5) and must then be followed by rapid energy loss (i.e. by internal conversion or vibrational relaxation from the excited state of the quencher). Unlike for many common fluorescent and phosphorescent molecules that are quenched by $^{1}O_2$ and $^{3}O_2$ respectively, ground state $^{3}O_2$ generally does not quench uranyl(VI) phosphorescence, however considerable vibrational overlap with the harmonics of high energy bond vibrations will result in the observation of quenching. Drobot \textit{et al.}\textsuperscript{14} quantified a dependence of uranyl(VI) lifetime on temperature. This study also reported the lifetimes for mononuclear uranyl(VI) aqueous hydrolysis species. The results are collated in Table 1-3. Interestingly, the effect of water quenching, which is commonly reported,\textsuperscript{46,47} appears relevant only until UO$_2$(OH)$_3$, which reflects the importance of other factors, such as proton abstraction and radical recombination in the excited state.\textsuperscript{48}

\textit{Table 1-3: A summary of the lifetimes reported for hydrolysis products of uranyl(VI). From reference 14}

<table>
<thead>
<tr>
<th>Aqueous species (water excluded)</th>
<th>Lifetime at 1 °C, 10$^{-8}$ M U(VI), 1 M NaClO$_4$. (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO$_2^{2+}$</td>
<td>10.2 ± 0.2</td>
</tr>
<tr>
<td>UO$_2$OH$^+$</td>
<td>44.9 ± 2.4</td>
</tr>
<tr>
<td>UO$_2$(OH)$_2$</td>
<td>78.9 ± 6.8</td>
</tr>
<tr>
<td>UO$_2$(OH)$_3$</td>
<td>3.4 ± 0.2</td>
</tr>
</tbody>
</table>

Other commonly reported quenchers are iron in mineral structures,\textsuperscript{49} carbonate\textsuperscript{50} and chloride.\textsuperscript{51} Due to the requirement for proximity (i.e. a collision) between the excited uranyl(VI) and the quencher, lowering the temperature of a lifetime measurement will reduce the rate of quenching and increase the observed lifetime. In addition, an increase in solvation is usually associated with a decrease in the observed lifetime.\textsuperscript{36}

With all of the above discussions considered, a reduction in the observed luminescence lifetime can occur via one or more forms of the following four primary interactions: (1)
A change in symmetry. For example, Billiard and Geipel\textsuperscript{31b} found that higher symmetry resulted in a decreased emission intensity, by observing the overall symmetry of uranyl(VI) carbonate complexes. Specifically, the observed emission intensity would increase when the resulting structure had reduced symmetry (i.e. $D_2h$ of $[\text{UO}_2(\text{CO}_3)_2\text{OH}]$), and the intensity decreased with increased symmetry (i.e. $D_3h$ of $[\text{UO}_2(\text{CO}_3)_3]$). (2) Vibrational and collisional quenching. Vibrational quenching involves the transfer of energy from the triplet excited state of uranyl(VI) to a vibrational excited state of an equatorially bonded sigma donor or proximal solvent molecule. Conversely, collisional quenching is heavily temperature dependent and involves the transfer of electronic energy during a collision of the triplet excited state of uranyl(VI) and that of a thermally energetic acceptor molecule. (3) Thermally activated back electron transfer processes from the uranyl(VI) excited electronic state to a higher lying excited state; a process which occurs if there is spectral overlap of the emission and absorption spectrum of the higher and lower lying states and if the energy difference between the donor and acceptor states is $<1850$ cm$^{-1}$\textsuperscript{44} This is similar to Förster resonance energy transfer (FRET) which commonly occurs in pairs of organic fluorophores which have complimentary photophysical properties. In other words, the emission of a donor must overlap with the absorption of the acceptor, the effect is inversely proportional to the proximity of the two emissive species.\textsuperscript{52} Although this effect has not been explicitly reported for two uranyl(VI) species, this may be possible for two neighbouring uranyl(VI) species, and this could be observed as a change or skew in the observed intensity of emission towards lower energy vibronic transitions. (4) Electron transfer processes. These processes result in a chemical change, for example, consider the excited triplet state $\text{UO}_2^{2+*}$ as a highly oxidising and reducing radical, which can undergo a multitude of chemical reactions with electron rich species.\textsuperscript{40} For example, Fe(II) is known to quench the excited state of uranyl(VI) and will facilitate its photo-induced reduction to U(IV).\textsuperscript{52b}

The breadth of potential interactions with competing effects on the lifetime, as outlined here, give rise to the often qualitative definition of the uranyl(VI) lifetime. It is therefore best utilised as a tool to expose change within an experiment where confounding variables such as experimental conditions are minimised.
1.4 Minerals

Minerals are ubiquitous in the environment, their structures form highly reactive metal oxide-aqueous interfaces upon hydration, resulting in acid-base, ligand exchange and or redox chemistry affecting the mobility of ions, such as solvated radionuclides (e.g. uranyl(VI)).\textsuperscript{53} The most relevant group of minerals in a GDF are clay minerals (smectites) such as bentonite (which is composed mostly of montmorillonite), which form reactive edge sites and interlayer interactions, as discussed in section 1.4.3. In order to approach the complex speciation of uranyl(VI) with clay minerals, the interaction with single mineral systems such as silicon oxides and aluminium (oxy)hydroxides are studied alongside that of the clays.

Clays are made from layers of silicon centred oxide tetrahedron, and aluminium centred oxide octahedron. The aluminium oxide octahedron layer is occasionally referred to as the ‘gibbsite-like’ layer.\textsuperscript{54,55} Gibbsite is a mineral made up of aluminium centred octahedral oxides. Bayerite and boehmite, an aluminium oxyhydroxide and an aluminium oxide mineral respectively, were included in this study for their similarities to this particular layer. Silica gel and quartz were selected to emulate the second type of layer, the silicon tetrahedron. Silica gel is amorphous whereas quartz is crystalline, both mineral phases, as well as semi-crystalline phases, are present in many montmorillonite clays.\textsuperscript{46,48}

Many other elements are present in significant quantities within clay structures i.e. iron or titanium. These can have a large effect on the sorption behaviour of uranyl(VI).\textsuperscript{1} These differences are more difficult to emulate, so two sourced clays with differing concentrations of the elements believed to most significantly affect sorption are considered. The sourced clay SWy-2, a montmorillonite, is frequently used in these types of studies,\textsuperscript{32,58,59} as well as the low iron montmorillonite, STx-1b.\textsuperscript{60}

Research into the behaviour of the interface between metal oxides and aqueous solution increased significantly during the 1990’s with the aim of improving the understanding of atmospheric chemistry, catalysis, environmental sensing, corrosion as well as environmental chemistry and geochemistry more generally.\textsuperscript{53} Several theories have been

\textsuperscript{1} For example, Payne et al. (reference 33) highlights the importance of small amounts of very reactive titanium oxide surfaces in kaolinite.
developed for describing the interface, such as the electrical double layer (EDL). An EDL forms whenever a surface is hydrated; due to the high di-electric constant of water the surface becomes charged and attracts an immovable layer of water molecules, referred to as the Stern layer (which is composed of the inner Helmholtz or β-plane and outer-Helmholtz or d-plane.). Further from the surface a second layer of attracted water molecules form to balance the remaining charge of the surface, the second layer is referred to as the diffuse layer or Gouy-Chapman layer. Cations and solvated cations will interact with these layers and the surface to different extents. Inner-sphere refers to the binding of specifically adsorbed ions, i.e. ions that sorb directly to the metal surface, and outer-sphere bonding as non-specifically absorbed solvated cations i.e. ions occupying the outer Helmholtz layer (see Fig. 1-6).

Fig. 1-6: Simplified schematic model of the Stern layer of the electric double layer (EDL) at the metal oxide-liquid interface. Arrows indicate the direction of charge (i.e. arrow head is negative). Adapted and re-drawn from Brown et. al.53
Also important is the change in the metal surface relative to the clean oxide surface, indeed even in air water forms up to 8 monolayers on the α-Al₂O₃ surface in the presence of 80% relative humidity at 300 K.¹ Thus a metal oxide surface is really a metal hydroxide surface. This is true for all metal oxides, but these properties become even more difficult to define for clays where the multitude of potential faces (i.e. (010) and (110) are commonly studied edge surfaces of 2:1 smectite clays) and metal substitutions in the octahedral or tetrahedral sheets need to be considered. Finally, a crystal surface will be covered in defects such as kinks, vacancies and adatoms (the opposite of a surface vacancy) (Fig. 1-7).

![Diagram of defects on a single-crystal surface](image)

*Fig. 1-7: Simple block diagram of defects on a single-crystal surface. Diagram reprinted from reference 53*

With this in mind, four key properties should be considered when determining speciation at the water-mineral interface (1) the structure of the minerals studied, including, where possible, the effect of water on the structure, and reactivity of surface sites; (2) the surface charge¹ and possible arrangements of hydroxyl groups; (3) the solution speciation, including changes in the solution species upon interaction with the solid surface (i.e. does the electric double layer result in further/reduced hydrolysis?); (4) the kinetics of sorption, which is generally fast (taking only hours for a silica gel)² but may take days (e.g. batch sorption experiments with clays are generally run for at least two days).³

¹ The surface charge relates to the behaviour of surface hydroxyl groups. There are two commonly used values to describe surface charge behaviour, the point of zero net charge (PZC) which is typically measured by titration, or the isoelectric point (IEP) determined by electrokinetic measurements. Discrepancies between the two can be large as the properties are fundamentally different, this becomes particularly true for clays - this is outlined in more detail in reference 202.
1.4.1 Mineral structures 1: Aluminium Oxyhydroxides

There are various aluminium hydroxide and oxide phases, the most thermodynamically stable is corundum ($\alpha$-Al$_2$O$_3$) of which there are various meta-stable oxides ($\gamma$, $\omega$, $\kappa$, $\delta$, $\psi$, and $Z$). The aluminium hydroxides are comprised of the monohydroxides (AlOOH) boehmite and diasopore and the trihydroxides (Al(OH)$_3$) gibbsite and bayerite. Gibbsite, like bayerite, has a pillared structure of close-packed oxygen atoms with aluminium atoms filling 2/3 of the octahedral sites between the two layers (Fig. 1-8). The stacking of the double layers is AB BA (bayerite is AB AB).

![Fig. 1-8: (a) View of a single layer of the structure of gibbsite looking down at the basal plane. (b) Side view of the gibbsite structure orthogonal to the basal plane. Al(red), O(blue), H(light grey). Reprinted from reference 64](image)

Gibbsite ($\gamma$-Al(OH)$_3$), boehmite ($\gamma$-AlOOH) and diasopore ($\alpha$-AlOOH) are the three principal oxohydroxides of alumina and are found in iron-rich lateritic or terra rossa soils and various sediments. Bayerite is in a metastable state, it is therefore very rare in nature. However, Lefèvre et al. found that $\gamma$-alumina (Al$_2$O$_3$) slowly transforms to bayerite after four days of hydration, and increases in concentration for up to approximately two months. When exposed to water vapour, an unhydrated alumina surface (e.g. corundum) reacts to form a hydroxyl group terminated surface, where the coverage of hydroxyls depends on the partial pressure of water. Eng et al. used X-ray based techniques and found the surfaces of hydrated alumina (Al$_2$O$_3$) to be more gibbsite like, and this was confirmed by simulations. This indicates that although bayerite is
rarely found in large quantities in nature, it is frequently found at the surfaces of aluminium oxides upon hydration, making it an important reference mineral in this research.

There are several types of surface hydroxyl groups and each can have very different chemical properties. The surface hydroxyl is defined by the ratio of hydroxyls to aluminium atoms (Fig. 1-9). For example, a single aluminium atom coordinated to multiple hydroxyl groups are removed between 500 and 700 °C and the single coordinated sites require temperatures above 700 °C to fully dehydroxylate.\textsuperscript{64}

\textbf{Fig. 1-9: A single layer of the boehmite structure showing the edge (right) and basal plane surfaces (top and bottom). a) Hydrogen bonded water at the edge surface. b) The edge-site hydroxyl groups. c) A singly coordinated hydroxyl group at the basal plane.}

For gibbsite and bayerite, the isoelectric point (IEP) is generally reported to be between 8.5\textsuperscript{71} and 10.\textsuperscript{72,73} i.e. at above a pH of 10, the surface is mostly negatively charged, and below a pH of 8.5 it is mostly positively charged, at zero ionic strength. For the doubly coordinated hydroxyls, a pK\textsubscript{a} of 2 to 4 is reported for the deprotonation of Al\textsubscript{2}-OH\textsuperscript{+}, whilst the singly coordinated edge sites are given the much higher pK\textsubscript{a} of between 8 and 10 for the deprotonation of Al-OH. This work uses a synthetic powder with micron-sized particles, so the area of the basal plane is low, therefore the dominant interaction is with mineral edge sites, which have the much higher pK\textsubscript{a}, and thus the main interaction is typically with that of a single coordinated hydroxyl (i.e. Al-OH).

\textbf{1.4.2 Mineral structures 2: Silica}

Silicon has four valence electrons and forms Si\textsuperscript{4+} upon oxidation, resulting in a network of SiO\textsubscript{4} tetrahedron (Fig. 1-10). If every oxygen atom is involved in a Si-O-Si bridge (hence chemical formula SiO\textsubscript{2}), the mineral is a form of quartz. Silica gel, on the other hand, also consists of SiO\textsubscript{4}-tetrahedron but with only a partial requirement for each oxygen to form Si-O-Si bridges. The resulting structure is amorphous with the unbridged
oxygen atoms being charge balanced by cations (usually protons) that were present in the solution from which the silica was formed. However, the unbridged oxygen atoms are relatively electron withdrawn owed to the high electron affinity of Si$^{4+}$, meaning that their free electron pairs are comparatively inactive and thus only weakly acidic. For example, the exchange of a $>$SiO-H proton with a metal ion is fast even at low pH. The $>$SiOH is also very unlikely to take on another proton (forming $>$SiOH$_2^+$). Silica gel can therefore be described as functioning as a weakly acidic ion exchanger.74

Fig. 1-10: Left: Silica tetrahedron unit displaying typical bond angle. Centre: 2D representation of 3D crystalline SiO$_2$ structure. Right: 2D representation of 3D amorphous silica structure.

Silicon oxides are ubiquitous in the environment.75 For example, amorphous silica is known to form on the surface of quartz in the presence of water and amorphous silica is also known to coat nanoparticles resulting in behaviour exactly like that of amorphous silica particles, particularly at alkaline pH.76 A form of silica gel is often observed in clays as interstitial opal and is a reasonable model for the tetrahedral layer unit of many clays. It also has an extremely high surface area (>480 m$^2$/g) and strong ion uptake character (≈4.75 sites/nm at low pH, and up to 10 times higher above pH 8 as pore spaces deprotonate) making it ideal for batch sorption.77

Due to the electron withdrawing nature of Si$^{4+}$, the pK$_a$ of surface silanol groups is expected to be low. Ong et al.78 found the pK$_a$ was split into two distinct values. By
studying the surface of quartz using SHG, the authors found the pKₐ for one silanol site (accounting for 19% of the total) to be ~4.5, and a second silanol site (accounting for the remaining 81%) had a pKₐ of 8.5 (Fig. 1-11).

Fig. 1-11: Surface potential of Quartz measured by SHG versus pH. Calculated using constant capacitance model (+); model independent calculation from SH data with a single reference point (O). Reprinted from reference 78

Somewhat in support of this finding, Keith et al. found the PZC to be <2.83, the silica surfaces posed very slight negative charge in the moderately acidic range (pH < 7), with significant dissociation of silanol groups above pH 7. The exact PZC for silica samples is difficult to define, the values are often so low that they are determined by arbitrary extrapolation. In any case, the PZC is very rarely above 3, and averages of several different forms of synthetic and natural silica and quartz samples are between 2.3 and 3.0.

1.4.3 Mineral structure 3: Clays

Clays and clay minerals refer to the phyllosilicates and include illites, kaolins and smectites. In this work the smectites, such as montmorillonite (Na,Ca)₀.₃₃(Al,Mg)₂(Si₄O₁₀), are the main focus because of their ubiquity in a diverse range of environments, including soils and sediments. Most clay minerals are formed

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¹ Second harmonic generation (SHG) is a particularly important method for measuring the acidity of surface hydroxyl groups as it is non-destructive. Electro-kinetic methods (i.e. electrophoresis or streaming current) are traditionally used to calculate these properties, however it applies a shear-stress to the surface, since silica gel appears to have a ‘soft’ surface (i.e. it deforms under shear stress) measuring its surface this way is likely to give inaccurate results. see reference 77 for a more detailed discussion.
by the gradual weathering and deposition of exposed rock.\textsuperscript{82} The actual definition of ‘clay’ varies, but they are no more than 4 µm in diameter and are generally plastic when hydrated.\textsuperscript{83}

Clay minerals are formed of octahedral (O) and tetrahedral (T) sheets (see Fig. 1-12). O sheets contain a cation centre such as Al\textsuperscript{3+}, Fe\textsuperscript{3+}, Mg\textsuperscript{2+} or Fe\textsuperscript{2+} and are surrounded by 6 oxygen atoms. Four of the oxygen atoms form sharing edges to connect neighbouring O. T sheets contain a cation centre, typically Si\textsuperscript{4+}, Al\textsuperscript{3+} and Fe\textsuperscript{3+}, but are bonded to four oxygen atoms. Three of these oxygen atoms bond to neighbouring T forming a basal plan of oxygen atoms, resulting in alternating apical oxygen atoms. A 1:1 structured clay consists of repeated O and T sheets, a 2:1 structure consists of one O sheet sandwiched between two T sheets. A 1:1 layered mineral will not generally expand to accommodate hydrated cations in its interlayers. However, between adjacent 2:1 layered structures, the interstitial region will expand to accommodate hydrated cations, in order to balance the negative charge between the adjacent T sheets.\textsuperscript{84}

\textbf{Fig. 1-12:} An image of the powdered clays montmorillonite and kaolinite with chemical formula and a simplified representation of the layered structure (see text). b) A simplified representation of the build-up of layers into particles and particles into aggregates. Note the inter-particle space between particles in an aggregate.

These layered structures stack up to form particles and particles group to form aggregates. This layering and aggregation affords regions within the clay where different local bonding can take place. The size of the interlayer, and the interactions of the cations
within it is determined by the level of hydration of the clay.\textsuperscript{85} Under greater hydration the cations within the clay interlayers can become nearly indistinguishable from solvated cations,\textsuperscript{86} with decreasing hydration resulting in greater influence from the oxide clay surfaces. The effect of drying loaded clays can affect the spectroscopic properties.\textsuperscript{87} Additionally, whether a clay is wet or dry will affect the optics of a luminescence measurement. The IEP of montmorillonites is generally very low, <3. With a PZC around pH 7.6.

Muscovite, KAl\textsubscript{2}(AlSi\textsubscript{3}O\textsubscript{10})(OH,F)\textsubscript{2}, is a 2:1 (TOT) phyllosilicate mineral\textsuperscript{1} known for its near perfect cleavage (001) basal plane. An aluminium O sheet is sandwiched between two silica T sheets, where one in every four silicon T are replaced by an aluminium T. The resulting negative charge from the aluminium substitution requires charge balancing from potassium cations, located in the interlayer region. Muscovite has a very difficult to define IEP, as it changes with time and the conditions under which the muscovite is kept, but one might expect it to be very low (i.e. <3), like similar clays.\textsuperscript{88}

Kaolinite is a 1:1 clay, meaning each sheet is composed of one T and one O layer. Kaolinite has a high proportion of edge sites, especially compared to muscovite. Kaolinite has an IEP <3, and a PZC around pH 6, although reported values vary widely, as is true for all clays.\textsuperscript{89} Crucially, in addition to a negligible interlayer interaction, kaolinite is recognised for having a modest titanium content (~2% by weight, conversely SWy and STX are 0.09% and 0.22%, respectively\textsuperscript{90}). Titanium replaces aluminium in the O units, and forms TiOH hydroxyls at edge sites, which tend to deprotonate at a lower pH than similar AlOH groups.\textsuperscript{33}

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1 Technically not a clay mineral, muscovite is a subclass of mica
Speciation of uranyl(VI) with geological media

Initially, research into the interaction of aqueous actinides with mineral surfaces was driven by the requirement for more accurate dissociation constants ($K_D$), the parameter essential to the performance assessment of GDFs. However, surface speciation and sorption mechanisms became necessary to develop the appropriate models and the field expanded into modern spectroscopic techniques such as Extended X-ray Absorption Fine Structure (EXAFS) and luminescence spectroscopy. EXAFS spectroscopy is the most widely used spectroscopic technique for speciation in this field. High energy photons (X-rays) ionise a core-electron and the resulting electronic rearrangement in the target nuclei results in the emission of photoelectron waves, which are effected by other scattering atoms nearby, creating a fine structure in the measured absorption coefficient. This technique is effective at determining atomic distances (information which is extremely valuable in speciation), but the assignment of the identified atoms can become difficult, especially for elements with similar atomic mass, such as aluminium and silicon. Some specific examples are provided in section 1.6. Luminescence, although unable to provide atomic distances, can be used to identify the elements involved, thus the techniques are complementary.

Luminescence is also very commonly reported for actinide mineral surface interactions. Cm(III) is a model actinide for investigation by luminescence spectroscopy, its intra-f-f emission is affected considerably by slight changes in the ligand environment and the lifetime indicative of the extent of hydration/complexation. Uranyl(VI) is much more complex. The speciation of uranium can be difficult to describe, owed in part to its complex aqueous chemistry. For example, with more advanced methods of measurement and interpretation, the aqueous speciation of uranium at low concentration was recently and significantly updated, despite this system containing just uranyl(VI) nitrate at a range of pH values.

Sorption to the surface of minerals, as outlined in section 1.4, can be broadly divided into outer-sphere or inner-sphere sorption. Outer-sphere sorption typically giving EXAFS spectroscopic responses similar to that of solvated uranyl(VI), and some literature suggesting the observation of similar luminescence properties between outer-sphere and bulk responses. Inner-sphere bonding is usually observed as bonding to
surface oxides in a bidentate fashion,\textsuperscript{32} and this is commonly supported by an observed splitting in the EXAFS equatorial shell interference pattern (typically denoted UO\textsubscript{eq}), into two surface hydroxyls and three water molecules.

Several other generalities\textsuperscript{1} are worth mentioning here, before the more comprehensive review of these interactions in section 1.6. Inner-sphere sorption is generally less reversible than outer-sphere. Outer-sphere sorption is largely independent of pH, but is dependent on the presence of competing ligands/complexants, the ionic strength (including the electrolyte composition) and uranyl(VI) concentration. Inner-sphere is determined by the state of amphoteric hydroxyl surface groups and thus, the pH. The order of oxide site strength is: aluminium > titanium > silicon. This corresponds to the valence coordination number ratio, defined by Pauling. Complexing ligands (e.g. carbonate) inhibit sorption by complexing with the metal or competing for sorption sites.

\textsuperscript{1} These generalities are gleaned from several recent reviews. See references \textsuperscript{3,5,163,203}
1.6 Literature on the interaction of uranyl(VI) and minerals

1.6.1 Aluminium oxides and uranyl(VI) interactions

The following is a chronological review of speciation literature regarding the interaction of uranyl(VI) with aluminium oxides. Section 1.4.1 provides an introduction to the structures of these minerals and a discussion of their properties.

Two $\gamma$-$\text{Al}_2\text{O}_3$ samples were studied by EXAFS spectroscopy,\(^\text{95}\) the first at pH 6.50 and the second at pH 3.48, the former had an initial uranium solution concentration $4 \times 10^{-5}$ M (99.9% uptake) and the latter had a much higher initial uranium concentration of $1 \times 10^{-2}$ (3.33% uptake), giving moles of uranium per g solid of $4.2 \times 10^{-5}$ and $3.3 \times 10^{-4}$ respectively. Both samples showed a splitting of the $\text{UO}_\text{eq}$ bond, suggesting the formation of inner-sphere bound species. The sample at pH 6.50 showed a U-U interaction at 4.0 Å with a CN of $\sim$0.4, suggesting a mixture of both polynuclear and mononuclear uranyl(VI) surface species.

Azenha et. al.\(^\text{96}\) reported the luminescence of uranyl(VI) sorbed to both an $\alpha$-alumina and $\gamma$-alumina (Fig. 1-13). They found them to have very similar emission spectra at low pH and low T (77K). Although no concentrations are given in the methods and mixtures were mixed for only 24 hours. The emission spectra are very similar, and display two major species that the authors believe correlate to Schoepite ($\text{UO}_3\cdot x\text{H}_2\text{O}$ where $1 < x \leq 2$) and a sorbed or hydrolysed species, but this is not discussed further.

![Fig. 1-13: Luminescence spectra at 77K ($\lambda_{ex} = 337$ nm) of uranyl(VI) sorbed from nitrate solution to (a) $\alpha$-alumina (pH 3.8) and (b) $\gamma$-alumina (pH 2.8). Reprinted from reference 96](image-url)
Catalano et al.\textsuperscript{97} studied the interaction of a polished surface of \(\alpha\)-\(\text{Al}_2\text{O}_3\) (1102) with a high concentration of uranyl(VI) (1 mM) at pH 5. The authors determined the stability of several surface functional groups using bond-valence theory. They found \(\text{Al}_2\text{OH}^0\) and \(\text{AlOH}^2+\) surface complexes to be stable, and \(\text{AlOH}^1/-2, \text{Al}_2\text{O}_2^1, \text{Al}_3\text{O}^1/-2\) surface complexes which may be stable at high pH. They then considered the coordination of uranyl to these surface complexes, using EXAFS results to guide the bond distances of the equatorial plane. The most stable complexes were \(\text{Al}_3\text{O}-\text{UO}_2\) and \(\text{AlOH}-\text{UO}_2\), with \(\text{AlO}-\text{UO}_2\) possibly stable at high pH. This form of modelling is unable to accurately consider bi-dentate binding, which was considered in a steric analysis. Considering the sterics, three sites for binding to the \(\alpha\)-\(\text{Al}_2\text{O}_3\) (1102) surface were proposed. (1) monodentate, mononuclear to \(\text{AlOH}^-\) sites, (2) bidentate, binuclear to adjacent \(\text{AlOH}^-\) sites, (3) bi or tridentate and mono- or dinuclear to \(\text{Al}_2\text{O}\) and one or two \(\text{AlOH}^-\) sites. (1) was found to be the best fit for crystal truncation rod (CTR) diffraction measurements and grazing incidence-EXAFS data. Crucially, this study differed significantly to (then) recent findings which found evidence for a bidentate assignment.\textsuperscript{98} They note this is probably because this study uses a single crystal, and most others use powders; in powders adjacent singly coordinated oxygen atoms are available for binding in much higher quantities. They also argue that the species they identify may not be observed in EXAFS measurements due to the large interatomic distances, resulting in large Debye-Waller factors and low coordination numbers, resulting in low signal-to-noise ratios.

Baumann et al.,\textsuperscript{99} studied the interaction of uranyl(VI) with gibbsite in the pH range 3.5 to 9.5 at 0.5 steps in air and mixed for less than three days. Luminescence is reported after excitation at 266 nm. Samples below pH 5 and above pH 8.5 are omitted from the results because the signal was too weak. The lifetimes between pH 5.0 and 8.0 were all fitted to a bi-exponential model, the lifetimes are averaged to give a \(\tau_1\) of 330 ± 115 ns and \(\tau_2\) 5600 ± 1640 ns, the lifetime for \(\tau_2\) was significantly longer than the other samples at 7260 ± 560 ns. They observe the short and long-lived luminescent species relate to the same emission band positions, and conclude that the two species must contain the same number of hydroxyl groups in the first coordination sphere. This is supported by Eliet et al.,\textsuperscript{100} who described changes in spectral features based on the number of
hydroxyl-groups. Thus, the two species should differ only in their water content. They also observe an increase in the intensity of emission of the second longer lived species with increasing pH. Citing X-ray absorption spectroscopy (XAS) studies, they identify the short lived species as a bidentate mononuclear inner-sphere surface complex, and the longer lived species as a polynuclear surface species, which has fewer water molecules in its structure than the shorter lived species. The water molecules are reported to quench the excited state of uranyl(VI) and thus the shorter lived species would have more ordered water molecules in its structure. They also concluded that the larger a polynuclear uranyl species, the longer its luminescent lifetime.

Froideval et al. studied γ-Al₂O₃ with uranyl(VI) under a dinitrogen atmosphere. They observed that the γ-Al₂O₃ transformed into gibbsite and/or bayerite after washing. This study did not observe a splitting in EXAFS measurements for samples between pH 4 and 5. Although they state this may be due to the short k-range used in the experiments. The emission is similar for all the samples studied but are represented by at least 3 distinct lifetimes. The authors offer a discussion of several possible complexes, this includes several outer-sphere complexes, i.e. a binuclear outer-sphere sorbed complex, as well as several inner-sphere complexes. Crucially, this study begins to highlight the shear complexity and multitude of possible surface complexes. They conclude that their spectroscopic results indicate that mainly, uranyl(VI) is sorbed to alumina by inner-sphere interactions, and that multiple uranyl(VI) complexes co-exist even at low uranium coverage of the available alumina surface.

Chang et al. studied the sorption of uranyl(VI) onto gibbsite from pH 4 to pH 8 without carbonate at three ionic strengths, 0.001, 0.1 and 0.4 M NaClO₄ and uranium concentration 8.4x10⁻⁷ M, allowed one week for sorption equilibration and studied the samples using TRLFS at 5K and at 415 nm excitation. The authors observe a red shift in the emission with an increase in the delay and the first main peak became more intense relative to the second. A much smaller peak at 480 nm also became more intense with

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¹ At this point, the authors cite Kowal-Fouchard et al. which studied a similar system at a much higher uranium concentration and which reported much longer lifetimes and in which these authors believe correlate to uranium solids and not sorption species.

² Although not the main focus of this review, the authors also observed that the sorption edge would shift depending on the g/L ratio, a higher ratio resulted in sharp edges at pH ~4, and a lower ratio would increase the sorption edge as high as pH 6.
increasing delay, but this peak does not red-shift and broaden with increasing pH, when all other lower energy peaks did. The authors then used evolved factor analysis (EFA) and multi curve resolution (MCR) in the Partial Least Squares (PLS) toolbox to resolve four species from the emission spectra. The four species were resolved and fit using Gaussian functions, the first three differences in vibrational energy were then averaged to determine the $E_{0,0}$ fundamental vibrational transition. Below pH 5.5, the species AlO-(UO$_2$)$^+$ dominates, and above pH 5.5 the species AlO-(UO$_2$)OH$^0$ dominates. A third species present at low ionic strengths is competitive AlO-(UO$_2$)$^0$ over pH range 5.0-8.6 (8.6 coincides well with the calculated PZC at an ionic strength of 0.001 M), believed to be an outer-sphere sorbed species (so identified due to its blue-shifted, aquatic-like emission spectrum) most likely [UO$_2$(OH)$_3$]$^-$.

Hattori et al.$^{105}$ used a combination of density functional theory (DFT) and EXAFS spectroscopy; the EXAFS samples were prepared in a dinitrogen atmosphere and at pH 5.6 and 9.7 and the solid used was a synthetic gibbsite. The EXAFS spectra showed no U-O$_{eq}$ splitting, but the authors reported large Debye-Waller factors, suggesting uncertainty in the reported distances. They also observe an oxygen atom at a U-O distance of 2.9 Å with a coordination number (CN) of 1.1-1.5. This bond is too long for a normal U-O$_{eq}$ interaction, and too short for a U-O$_{as}$ multiple-scattering path. The multiple-scattering path does overlap somewhat with the U-Al bond located at 3.36-3.39 Å with a CN of 1.4 to 2.0. These values are slightly longer than those reported by Arai et al.$^{106}$ whom studied an inner-sphere complex bound to imogolite (an aluminosilicate), and slightly shorter than those of montmorillonite reported by Hennig et al.$^{107}$ Finally, a U-U backscatter path was found at ~4 Å, suggesting the presence of polynuclear species or surface precipitates. The DFT studies performed by the authors show that sorption to the basal plane of alumina is not energetically competitive. They then found that both corner sharing and edge-sharing sites were almost equally energetically competitive, suggesting the presence of both species (See Fig. 1-14)

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$^1$ The averaging of these spacings may be problematic, after all the spacings are contracted with an increasing $\nu$ by the anharmonic oscillator, this contraction may be smaller than the error produced in this method, but it may be significant. If it is significant then $E_{0,0}$ will be undervalued.
Fig. 1-14: Six aluminium centred octahedron (blue) form a hexamer cluster and present bonding to uranyl(VI). Uranium(VI) atoms = grey, oxygen atoms = red, hydrogen atoms = pink. Overall image is the optimised structure of the corner- and edge-sharing configuration next to each other. Image reprinted from Hattori et al.\textsuperscript{104}

Nero \textit{et al.}\textsuperscript{108} studied the interaction of $\alpha$-alumina colloids with uranyl(VI) and phosphate by luminescence spectroscopy. The authors found that the presence of phosphate increases the uptake of uranyl(VI) and enhances the intensity of the emission. Furthermore, the samples, which varied in uranyl(VI) concentration, phosphate concentration and pH, exhibited similar emission characteristics, indicating a single sorbed coordinating environment. The results indicated the formation of surface precipitates of uranyl phosphate, with at least 4 distortions, in-homogeneities or varying number of fixed water molecules, as indicated by 4 unique lifetimes.

Müller \textit{et al.}\textsuperscript{109} investigated the formation of bayerite/gibbsite like surface features on Al$_2$O$_3$, but did not observe the formation of any IR bands known to relate to bayerite or gibbsite AlOOH bending modes. Regardless, in-situ IR of Al$_2$O$_3$ loaded with uranyl(VI) resolved three species as a function of surface loading; a monomeric inner-sphere
bidentate uranyl-carbonate species at low coverage, an oligomeric surface complex at modest coverage and a surface precipitate (schoepite-like) at high coverage.

Mei et al.\textsuperscript{110} conducted kinetic studies, which showed rapid uptake of uranyl(VI) to the Al\textsubscript{2}O\textsubscript{3} surface which plateaus within 3 hours, after which time the uranyl(VI) does not increase or decrease in retention. This suggests a strong chemical/inner-sphere interaction with the surface, as opposed to a physical/outer-sphere interaction.

### 1.6.1.1 Conclusions for literature assessment of uranyl(VI) and aluminium oxides.

The literature surveyed above suggests that the sorption of uranyl(VI) to aluminium oxide surfaces is complex and includes outer-sphere and inner-sphere, mononuclear and polynuclear and/or precipitated complexes. Inner-sphere complexes are the most commonly reported, of these the dinuclear bidentate, mononuclear bidentate and mononuclear monodentate complexes were all frequently observed. Some correlations can be drawn, with the most significant variables being pH, surface coverage and ionic strength. Lower pH and lower surface coverage correlate with mononuclear and monodentate species, whilst higher pH and higher surface coverage correlate with dinuclear and bidentate species. At low ionic strength outer-sphere complexes are more competitive but remain a minor component. These observations and correlations mostly serve to highlight the inherent complexity and range of surface complexes that form at the aluminium oxide surface.

### 1.6.2 Silicon oxides and uranyl(VI)

In 1992 Dent et al.\textsuperscript{62} published the first EXAFS study of both uranyl(VI) in solution and uranyl(VI) sorbed to clay or silica colloid/fine fractions. The authors anticipated that the uranyl(VI) would sorb via an exchange mechanism to the clay and via an inner-sphere sorbed species to the silica. The samples studied contained chloride, ammonium hydroxide and nitric acid and were acidic with a final pH of ~3 and ~5. Uranium concentrations were high, ranging from 0.01 to 0.05 mol dm\textsuperscript{-3} to 10g/L silica solid.

They also measured lower uranium concentration samples to assess the uptake to silica colloids - they found that most of the uranium is removed from solution by the silica at
and above pH 5 (see Fig. 1-15), but at a lower value of pH 4 for the clay (<2 µm, SWy-1).

![Graph showing the uptake of uranium as a function of pH.](image)

**Fig. 1-15:** The uptake of uranium at a total concentration of $10^{-6}$ mol dm$^{-3}$ onto silica colloid as a function of pH. Reprinted from Dent et al.$^{52}$

EXAFS spectroscopy of the pH ~3 and ~5 samples was qualitatively analysed. But a UO axial bond (UO$_{ax}$) of 1.81 Å was reported at pH 5 – the two silica samples are ‘essentially the same’ and have a likeness to an amorphous hydrous oxide precipitate sample.

Uranyl(VI)-silica luminescence assessments had been published at least as early as 1984,$^{111}$ with a focus on silica’s luminescence enhancement as a means for determining uranium concentration at trace levels. However, significant findings and discussion as to the use of luminescence for the speciation of uranyl(VI)-silica sorption were published in 1996 by Lopez et al.$^{112}$ They note the observed improvement in quantum yield of emission from an acidic uranyl(VI) solution (a $\Phi \sim 0.1\%$),$^{113}$ due to quenching by water molecules,$^{46}$ compared to uranyl(VI) sorbed to silica by reporting molar absorptivity increases from 9.0 to 24.4 dm$^3$mol$^{-1}$cm$^{-1}$ from perchloric acid solution to colloidal silica solution. Lopez used a 337 nm excitation wavelength and measured the emission spectra at 25°C and at pH 9 and a high uranium concentration of 0.67 mmol dm$^{-3}$. They observed large luminescence ‘scattering’ from the silica itself, which was collected and subtracted using a blank. Lifetime measurements of the uranyl(VI) loaded samples were
fit to a biexponential decay, comprised of a major component of 240 µs and minor component of 55 µs. The minor component disappeared after 1.5 hours. When the silica was dried it had no effect on the recorded lifetimes. Isotherm data published in the same year\textsuperscript{114} proposed and provided evidence for a two-phase surface mechanism. The adsorption process, they conclude, is controlled by two main phenomena (originally proposed as part of a 4-phase mechanism by McKay\textsuperscript{115}) (1) solute transfer from the boundary film to the surface of the adsorbent (rate = $10^{-7}$ to $10^{-5}$ m min$^{-1}$) and (2) transfer from the surface to the intraparticle active sites (rate = $10^{-8}$ to $10^{-7}$ m min$^{-1}$).

In 1998 Reich \textit{et al.} published new EXAFS spectroscopy results of the uranyl(VI) silica sorption system,\textsuperscript{116} of particular interest was a sample at pH 4.5 at the lower uranium concentration of 2x10$^{-5}$ M, 99% uptake onto 5 mgU/g solid, this sample was at the detection limit for EXAFS spectroscopy at the time and is therefore the noisiest and most difficult to model. Despite all higher loading samples fitting well to a UO$_{eq}$ splitting of 2.26-2.29 Å and 2.50-2.52 Å, this sample had a single UO$_{eq}$ shell at a distance of 2.26 Å with a coordination number (CN) of 2.6(4), a U-Si bond was also inferred at a distance of 2.72 Å, CN 0.5(4). They concluded that this indicated a polyhedral edge sharing interaction with the silica that is both inner-sphere and mononuclear. This finding is somewhat surprising as a U-Si bond of 2.72 Å is much shorter than that of any known U-Si bonds in U-Si minerals such as soddyite or uranophane (typically 3.16-3.17 Å). This was later the subject of an ab initio study at the MP2 level which found comparable U-Si distances of 2.88 Å for the geometry optimised uranyl(VI)-monosilicate (UO$_2$SiO$_4$H$_2$).\textsuperscript{117}

Sylwester \textit{et al.} (2000)\textsuperscript{95} and Gabriel \textit{et al.} (2001)\textsuperscript{118} exposed some of the changes in behaviour as pH is raised above pH 6, using EXAFS and TRLIF spectroscopies, respectively. Although Sylwester used very high loading concentrations (~13,000 ppm), EXAFS spectroscopic results showed a significant change in behaviour of a sample at pH 3.14 to that of a sample at pH 6.46. The low pH sample showed a UO$_{eq}$ splitting, but no evidence of local Si or U atoms. The high pH sample gave UO$_{eq}$ splitting, as well as a U-Si bond distance of 3.08 A, CN 0.97 and a U-U bond at 3.97 Å, CN 1.79. Gabriel, using much lower loadings (less than 1000 ppm in some samples), identified two major uranyl(VI) species from their lifetimes, 170 ± 25 µs at low pH (postulated as SiO$_2$UO$_2$)
and 360 ± 50 at high pH (as SiO$_2$UO$_2$OH). As this was conducted in the presence of CO$_2$, they also postulated the presence of a third ‘silent’ species around pH 8 and 9, which they predict to be =SiO$_2$UO$_2$OHCO$_3$$. Somewhat in support of this, several room-temperature-silent uranyl(VI) carbonate species were later identified by cryo-temperature luminescence.$^{119}$

Kowal-Fauchard et al. (2004)$^{120}$ published an ambitious luminescence based investigation into the sorption of uranium to montmorillonite, which included sorption to silica gel and bayerite. The study identified three uranium silica species by lifetime analysis, despite identifying only two unique emission spectra. The lifetimes were 65 ± 6 µs, 180 ± 20 µs and 400 ± 30 µs, the third only appearing at higher pH. These species are assigned as UO$_2$H$_3$SiO$_4$$^+$ on SiO$_2$, UO$_2^{2+}$ on SiO$_2$ and (UO$_2$)$_n$(OH)$_m$(2n−m)$^+$ on SiO$_2$, which is rather contrasting to previous work. However, these findings were later corroborated by Drot et al. (2007).$^{121}$

Chisholm-Brause (2004)$^{87}$ explores the underlying features and concepts involved in the sorption of uranyl(VI) to several surfaces, including silica. As previous studies had shown, they reported a significant change in the emission properties between a sample prepared at pH ~5 and another at pH ~8, the increase in pH is associated with a shift in the emission down in energy of ~215 cm$^{-1}$ for the first vibrational resolved peak. The proposed speciation was SiO-UO$_2^+$ at pH ~5 and SiO-(UO$_2$)$_3$(OH)$_5$ at ~pH 8. This is a notable departure from the mono-uranyl(VI) complexes for the higher pH species proposed in the majority of previous work.

High Energy X-ray Scattering (HEXS) requires higher concentrations (mM) than comparable XAS techniques, but it can provide atomic information over much greater distances. Soderholm et al. (2008)$^{122}$ presented HEXS data for several uranyl(VI) (0.05 M) and sodium metasilicate samples at various pH values. They found UO$_{ax}$ and UO$_{eq}$ bond lengths of 1.74 Å (wet) and 2.41 Å (wet), respectively, which are comparable to XAS data (see reference $^{120}$). At greater distances they found evidence of oligomerisation at and above pH 4, and clear single-crystal like behaviour above pH 5. Several bond lengths are proposed for various atomic arrangements and are summarised in Fig. 1-16.
Batuk et al. (2011) studied uranyl(VI) sorbed to silica gel nanoparticles and identifies SiO$_2$UO$_2$ and (SiO)$_2$UO$_2$OH, which corroborates much of the pre-2001 work cited here, but is in contrast to much of work in the years 2001 - 2010. Several techniques are employed to postulate this speciation (especially TRLIF at $\lambda_{ex} = 266$ nm and EXAFS spectroscopies). However, sorption experiments were completed in only 30 minutes, the work uses $^{232}$U (uranil(VI) sorption to silica has been shown to depend in part on the isotope of uranium used) and was conducted at high uranyl(VI) concentrations (10 to 100 µM). Small angle X-ray scattering (SAXS) and transition electron microscopy (TEM) results showed the uranyl(VI) to be sorbed homogeneously to the surface of the silica nanoparticles without formation of precipitates. Emission spectra are not observed to change over the full pH range, the authors noted this as unusual. Lifetime analysis identified two major species at values 49 ± 9 µs and 200 ± 24 µs. EXAFS data showed a consistent splitting of the equatorial oxygen atoms, with slight increases in the distance from uranium to the second equatorial oxygen atoms with increasing pH (pH 4.7 U-O$_{eq2}$ = 2.42 Å, pH 6.5 U-O$_{eq2}$ = 2.50 Å). Considering all this, they conclude that two structurally similar uranium species with different lifetimes are present on the silica surface. Both are bidentate coordinated with two Si atoms that differ in H$_2$O and OH.
coordination. They suggest that the species which has an extra OH instead of H\textsubscript{2}O is the longer lived species.

Ilton et al. (2012)\textsuperscript{124} reported cryogenic (6 ± 2 K) TRLFS measurements of uranyl(VI) to study the changes in speciation to a fine quartz surface at pH 6.0, 7.0 and 8.0 and over time (Fig. 1-17). Experiments were conducted in the presence of CO\textsubscript{2} and TRLFS measurements used \(\lambda_{ex} = 415\) nm. They identify two major fluorescent species \(a\) and \(b\). Species \(b\) is red shifted with respect to \(a\) by \(~7\) nm in the first peak position. Species \(b\) also has a longer lifetime, although lifetimes are not explicitly reported, it is evidenced by a red shift as the delay time is increased for a sample at pH 7 after 7 days. Curiously, species \(a\) and \(b\) are loosely defined by curves with peaks within limits ranging from 1 nm to 2.5 nm from a defined value. These curves are established by subtracting spectra with long delays from spectra with short delays, previous work had also used this methodology.\textsuperscript{104,125} No further assessment is conducted on the curves, such as the fitting of peaks or calculation of vibrational spacings, other than to observe the increasing relative intensity of species \(b\) with both increasing experiment time (from 1 to 41 days) and pH (from 6 to 8). Regardless, the curves are used to inform a very detailed discussion into the speciation of \(a\) and \(b\). Species \(b\) is assumed to be more tightly bound to the surface of the quartz. The authors establish, citing molecular dynamics studies\textsuperscript{126,127} and SHG\textsuperscript{128} studies, an argument for a molecular progression from a monodentate (species \(a\)) to bidentate (species \(b\)) silianol surface complex. The authors also note that the aqueous concentrations of Si indicated the presence of amorphous silica, which may contribute to the observed changes in sorption i.e. from micro- to nano-sized pores.\textsuperscript{129} They conclude however, on the transition towards a bidentate complex (species \(b\)) as being largely responsible for a much stronger interaction, which is harder to remove using nitric acid or carbonate solutions.
Massey et al. (2014)\(^{130}\) reported EXAFS spectroscopy of a synthetic uranyl(VI) silicate from sodium metasilicate and uranyl(VI) acetate at pH \(\sim 5.6\). Results corroborate the findings from Sylwester\(^{95}\) and Soderholm,\(^{122}\) a U-Si distance of \(\sim 3.1\) to \(3.2\) Å indicating uranyl(VI) is coordinated to silica in an edge-sharing bidentate, mononuclear geometry, and a U-Si distance of \(\sim 3.8\) - \(3.9\) Å indicating uranyl(VI) coordinated to silica in a corner-sharing bidentate, binuclear geometry.

Wang et al. (2015)\(^{131}\) studied uranyl(VI) binding to silica via periodic DFT and \textit{ab initio} MD. The work discusses two major bonding modes akin to inner-sphere (‘via chemical bonding’) and outer-sphere (‘via hydrogen bonding’), Fig. 1-20 presents all possible bonding modes. For the inner-sphere bidentate (a in Fig. 1-20) the U-Si bond distance was reported as \(2.97\) Å, close, the authors conclude, to the experimental value from Reich et al.\(^{116}\) of \(3.1\) Å, the shortest U-Si bond in the bidentate binuclear case (d in Fig. 1-18) is \(3.63\) Å. Bader charge calculations were then carried out to determine the extent

\footnotesize

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{example_image.png}
\caption{Normalized cryogenic TRLFS emission spectra of uranyl(VI) sorbed on quartz at a series of delay times. Sample is at pH 7, 7 days contact time, \(\lambda_{\text{ex}} = 415\) nm. Labels correspond to delay times, a: 0µs – 100 µs; b: 100µs – 300 µs; c: 100 µs – 600 µs; d: 100 µs – 1200 µs; e: 100 – 1800 µs; f: 300 µs – 2500 µs; g: 300 µs – 3500 µs. Reprinted from Ilton et al.\(^{124}\).}
\end{figure}
of protonation on the silica. They found deprotonated silica to be strongly preferred, however, at low pH and low temperatures, sorption to the protonated surface becomes very possible. They conclude that at higher pH, the fully deprotonated bidentate complex (a and d in Fig. 1-18) are preferred. Under more acid conditions, the monodentate and bidentate complexes display similar stability (a, d and g in Fig. 1-18).

Fig. 1-18: Optimized adsorption structures of uranyl(VI) adsorbed on the hydroxylated α-SiO₂(001) surface. Inner-sphere: bidentate complex (a) SiOO, (b) SiOH, (c) SiOHOH, (d) SiO-SiO, (e) SiO-SiOH, (f) SiOH₂SiOH; monodentate complex (g) SiO, (h) SiOH. Other-sphere complex (i). Colour scheme, U(blue), O(red), Si(orange), H(white). Reprinted from Wang et al.131

Comarmond et al. (2016)132 used a combination of ATR FT-IR spectroscopy, TRLIFS and surface complexation modelling (SCM) to study uranyl(VI) bound to SiO₂ in the presence of phosphate, but included samples without phosphate. They found uranyl(VI) forms two binary surface species. They note that the surface species >SiO₂UO₂ and >SiO₂UO₂OH are the most likely, but do not specify the nature of the bonding in any great detail. The approximate position of the emission bands correlate well with the
speciation made by Gabriel (2001), the decomposition methodology for identifying uranyl(VI) emissive species matches that employed by Ilton and other authors, despite some negative intensity in the emission on close inspection of the published deconvoluted spectra (see above in Fig. 1-17, and figure 3 of Comarmond) which presents a challenge.

1.6.2.1 Summary

Based on the literature covered, it is in this author’s view that the strongest evidence is in favour a two-species system for the full range of pH values under consideration. Both species are inner-sphere bound and in equilibrium with one another. The first species to form on the silica surface, which is also favoured at low pH, is less energetically favourable, or less tightly bound, than the second species. It would appear that with time, and with an increase in pH, the more energetically favourable, second species, becomes more dominant. The evidence for the true nature of the bonding of these two species however, is largely inconclusive and contradictory.

Despite the significant progress in understanding the sorption of uranyl(VI) to silica, there remains substantial confusion by the meaning of the luminescence data produced, perhaps caused by unsuitable data analysis. The purpose of luminescence in these studies should be to obtain accurate vibrational fine structure information and thus meaningful vibrational spacings, which can be compared to Raman data, or QM calculations. It has also been overlooked as to the information encoded in the excitation spectrum for these sorption processes, which may provide a direct probe into the vibrational character and thus chemical structure of the ligand environment.

1.6.3 Montmorillonite clays and uranyl(VI).

As with silica gel, the first major attempt to define the speciation of uranyl(VI) adsorbed to montmorillonite SWy-1 (herein clays are referred to by their source, i.e. SWy) was in 1992. Dent et al. recorded the EXAFS spectrum of a batch sorption sample at pH 4. The sample was modelled by a single UO\(_{eq}\) shell with CN 6.0 at a distance of 2.39 Å. The authors also detected a carbon atom at a U-C bond length of 2.93 Å. Based on the pH and model, the complex is likely hydrated uranyl(VI) within the interlayer. However, the carbon atom makes this result unclear since carbonate is not expected to be present
in solution at any appreciable concentration at such a low pH, suggesting an alternative model of the data may have been more appropriate.

Two expansive studies followed in 1994. Chisholm-Brause et al.\textsuperscript{133} published the first in a series of papers exploring the luminescence, XAS and sorption data of uranyl(VI) bound to SWy-1. They identified three separate sorption species, each with a single UO$_{eq}$ shell, but with distinct bond distances. The authors suggest that the first species to form at low uranium concentration and low pH would be to the most reactive site. Amphoteric edge sites\textsuperscript{i} are considered the most reactive and occupy between 5-15% of the total exchange capacity, the two remaining complexes are tentatively assigned to fixed charge sites, i.e. those within the interlayer. In the same year, Morris et al.\textsuperscript{94} (from the same research group) studied uranyl(VI) and SAz-1\textsuperscript{ii} using Raman and luminescence spectroscopies. The authors identify four distinct uranyl(VI) sorption species within the pH range 2.0 to 6.0 at variable ionic strength [I] and uranium loading, based on their emission and Raman properties. Initially, uranyl(VI) takes up amphoteric edge-sites until uranyl(VI) concentrations exceed the number of available edge sites, at which point uranyl(VI) occupies fixed charge sites. All four species are monomeric, and variation in specific chemistry edge-sites (i.e. bound to aluminol or silanol) may give rise to some of the observed changes in electronic and vibrational properties, the authors conclude.

Mckinley et al.\textsuperscript{134} studied the kinetics of uranyl(VI) sorption to SWy, gibbsite and silica in the absence of CO$_2$ within the pH range 4.0-8.5. The authors concluded that parameters derived from gibbsite may not be representative of aluminol at montmorillonite edge sites. Furthermore, their model calculations indicated three major surface complexes: UO$_2^{2+}$ bound to interlayer sites, UO$_2^{2+}$ bound to AIOH sites and a third complex which becomes significant over pH 6, (UO$_2$)$_3$(OH)$_3^{3+}$ bound to SiOH.\textsuperscript{iii}

\textsuperscript{i} Depending on the author, the different sites are given different names. Generally speaking, there are two major classes of site at montmorillonite. The first is an interaction at the interlayer where uranyl(VI) maintains at least the first hydration sphere (i.e. 4-6 water molecules), sometimes referred to as (cation) exchange sites, bonding to fixed charge sites, the basal plane, or an outer-sphere complex. The second is an interaction with the edge sites of the clay, sometimes referred to as bonding to amphoteric edge sites, or inner-sphere complexation.

\textsuperscript{ii} SAz-1 is a smectite and contains much less quartz or opal than STx and SWy, but considerably more phases (as identified by XRD) see reference 57.

\textsuperscript{iii} This study, and many others from the 1990’s and early 2000’s use uranyl(VI) aqueous chemistry to aid the determination of uranyl(VI) adsorption, e.g. as polynuclear species form in solution as pH is increased, uranyl previously bound to surface exchange sites becomes uncompetitive with monovalent electrolyte cations (i.e. Na$^+$). This kind of duality in solution and sorption chemistry is rarely observed in modern spectroscopic assignments.
Two samples from a study published in 2000 are of note. Sylwester et al.\textsuperscript{95} used EXAFS spectroscopy to study SAz-1 open to CO\textsubscript{2} at 0.1 M NaCl and with final pH values of 4.06 and 6.41 with uranium loadings of 1.09x10\textsuperscript{-5} M and 7.44x10\textsuperscript{-5} M, respectively. The sample at pH 4.06 showed a single UO\textsubscript{eq} distance of 2.41 Å with a CN of 6.35, the sample at pH 6.41 however, was modelled to two UO\textsubscript{eq} shells, the first at 2.30 Å and CN of 2.97, the second at 2.48 Å and a CN of 2.72. The pH 4.06 complex was therefore assigned to an outer-sphere complex, and the pH 6.41 sample as an inner-sphere mononuclear surface complex. This differs significantly to the results of similar work two years later where Hennig et al. reported EXAFS spectroscopy of uranyl(VI) with Na-STx in carbonate free conditions at various uranium loadings and pH values of 5, 6 and 7. They found that all samples were modelled well by a single UO\textsubscript{eq} shell with a CN of 6, with a U-Al bond with a distance between 3.40 and 3.44 Å with CN 0.6-0.8. They use this information to identify the binding as inner-sphere mononuclear bidentate to aluminol groups, despite the lack of a split equatorial plane.

Chisholm et al. published two further, comprehensive, investigations of uranyl(VI) bound to SAz\textsuperscript{135} and SWy\textsuperscript{87} with conclusions drawn primarily based on their luminescence properties. Both studies reported four species with considerable logical reasoning for assignments. However, some of the assignments received significant criticism from Catalano et al.,\textsuperscript{32} on the grounds that non-equivalent uranium atoms would be present in the proposed trimeric sorption complexes. Each atom of uranium in such a complex would give rise to individual lifetimes, and therefore appear as separate complexes. Catalano reported EXAFS spectroscopy results of samples at pH ~5.5 between low (0.001 M) and high (1 M) ionic strengths [I]. It was found that ~90% of uranyl(VI) is bound to exchange sites and 10% to edge sites at low [I], whilst at the same pH and high [I], 100% of the uranyl(VI) was bound to edge sites, stressing the importance of [I]. The authors also report monomeric uranyl(VI) carbonate species will predominate at high pH and/or high [I] to edge sites, first to Fe(O,OH)\textsubscript{6} sites and then Al(O,OH)\textsubscript{6} sites.
Schlegel et al.\textsuperscript{58} reported uranyl(VI) uptake onto montmorillonite (SWy-1) and hectorite\textsuperscript{1} and excluded carbonate. Sorption isotherms were reported along with two EXAFS samples, one from batch sorption with hectorite and a second from batch sorption with SWy-1. The montmorillonite sample (pH 6.61) showed a splitting in the equatorial shell and a U-Al/Si bond, this combined with results from Arai et al.\textsuperscript{106} suggested the Al/Si ambiguity could be reduced to Al, as such the authors proposed the model as in Fig. 1-19.

![Fig. 1-19: Proposed model of uranyl(VI) bound to the edge site of montmorillonite at pH 6.61. Reprinted from Schlegel et al.]({}"filename")

A few more studies offered useful observations in the following years. Bachmaf et al.\textsuperscript{136} provided several updated complexation values based on kinetic studies over a wider range of ionic strengths. Wang et al.\textsuperscript{137} reported several high resolution cryo-emission spectra for uranyl(VI) sorbed to several different mineral samples, including SWy. However these were conducted in the presence of CO\textsubscript{2} and at a single pH value of ~8.1 (although this may not be the final pH after batch sorption).

Fernandes et al.\textsuperscript{138} provide greater detail into alkaline conditions by presenting the EXAFS of uranyl(VI) sorbed to SWy in the absence and presence of CO\textsubscript{2} at pH 8. The EXAFS samples are modelled well by a split in the UO\textsubscript{eq} bond distances consistent with many previous studies. However, the results found little difference between samples with or without CO\textsubscript{2} and concluded that EXAFS may not be capable of resolving carbon

\textsuperscript{1} Hectorite is a rare 2:1 clay made up of silica absent in aluminium, its octahedral layers are made up of Mg or Li.
atoms at the expected distance of ~2.9 Å from the uranium atom. The authors also found that Si/Al distances of approximately ~3.09 Å and ~3.29 Å or Fe at ~3.42 Å provided reasonable improvements to the data, however no distinction could be made between Si, Al or Fe. This paper refers to a 2-site surface complexation model known as 2SPNE SC/CE. It creates a duality between the edge sites of montmorillonite, and defines them as strong or weak. Strong sites have a relatively low capacity for sorption and form surface complexes resistant to further changes to the aqueous conditions, weak sites have a much larger capacity but complexes formed are more labile.\textsuperscript{139} The 2SPCNE SC/CE modelling found that UO$_2$, UO$_2$OH, UO$_2$(OH)$_2$ and UO$_2$(OH)$_3$ are all competitive in sorption to montmorillonite strong sites in the absence of carbonate, and that weaker sites did not present a significant contribution.

Kremleva \textit{et al.}\textsuperscript{140,141} provide periodic density-function theory models of uranyl(VI) sorption at the edge sites of montmorillonite. The authors identify the incongruity between EXAFS and luminescence data: between pH 4 and 5 of uranyl(VI) on montmorillonite, luminescence identifies two species\textsuperscript{58} whereas EXAFS identifies one.\textsuperscript{120} Kremleva defines the surface based on the cut, treating the (010) and (110) surfaces in turn, the various oxides are then considered and summarised in Fig. 1-22. The five complexes correlate well with EXAFS bond distances, and all are of similar total energies. The authors therefore conclude that all complexes exist in equilibrium with one another.
1.6.3.1 Summary of uranyl(VI) sorption to montmorillonite clays

From the literature survey a few findings are reported consistently. For example, aluminol sites are reported to have a greater reactivity towards uranyl(VI) than silanol sites. Uranyl(VI) binds via exchange mechanisms at low ionic strength and/or low pH. Uranyl(VI) binds via inner-sphere mononuclear bidentate complexation with the edge sites of smectites when pH is $>\sim 5$, or uranyl(VI) concentration exceeds $\sim 35\%$ of the
maximum CEC of the montmorillonite, or the ionic strength is increased to >~1 M, with the final point requiring that the pH is >~4.

In the presence of carbonate and above neutral pH, uranyl(VI) tricarbonate complexes form at edge sites as above,\textsuperscript{137} but are likely remobilised with increasing pH, i.e. at pH 9 only 20-40\% remains sorbed.\textsuperscript{136} In the absence of carbonate, above neutral pH, the complexation at the surface of montmorillonite is not well understood. Trimeric complexes as proposed in the 1990s and 2000s by several authors\textsuperscript{87,133,134} is unlikely, however other analysis i.e. by EXAFS spectroscopy, is either ambiguous or inconclusive at the range necessary to improve understanding.

1.6.4 Other minerals

A summary of 12 pertinent selected publications which examine the absorption of uranyl(VI) to kaolinite (KGa-1b) follows. Uranyl(VI) sorbs to kaolinite at and over ~pH 3 and has a gradual sorption edge to ~pH 5, at which point sorption is close to 100\%, provided uranium concentrations are \(\leq 1\times 10^{-4}\) M. This is notably lower than montmorillonite minerals. Above neutral pH, carbonate, if present, will favourably complex with uranyl(VI), resulting in the remobilisation of uranyl(VI) into solution. In the absence of carbonate, uranyl(VI) remains sorbed to at least pH 10. Additionally, unlike other clays, there is no dependence on ionic strength. Also, unlike other clays, kaolinite appears to be capable of taking up much more uranium, believed to be a result of the much higher occurrence of edge-sites.\textsuperscript{33,34,136,142,143} According to XAS results,\textsuperscript{142,144,145} uranyl(VI) bound to kaolinite in the absence of CO\(_2\) forms a surface complex with a single UO\(_{eq}\) shell and silica or aluminium as a second neighbour below pH 8. Above pH 8 a trimeric uranyl(VI) surface species may form which is most likely (UO\(_2\))\(_3\)(OH)\(_5\). The trimeric complex was postulated by other authors,\textsuperscript{146} but not considered in computational models (MM\textsuperscript{34,147} or QM\textsuperscript{148,149}) or observed by luminescence spectroscopy.\textsuperscript{145} The fact that no split is observed in the equatorial shell by EXAFS spectroscopy has not stopped authors from assigning inner-sphere sorption complexation to the edge sites, indeed quantum mechanical studies have shown that UO\(_{eq}\) distances to surface sites can be comparable to UO\(_{eq}\) distances to water molecules.\textsuperscript{148} One study identified TiO\textsuperscript{-} surface sites to be very significant, especially at low uranium concentrations.\textsuperscript{33} However, this has not been observed or discussed by
other authors. Edge-sites are widely expected to be much more significant than the basal plane and this is confirmed by QM calculations. However several potential adsorption complexes involving slightly different surface sites were found to be at similar total energies, suggesting that several sorption complexes may coexist at the kaolinite edge, these differences may be missed by XAS, but detected by luminescence lifetime measurements.

Uranyl(VI) sorbed to muscovite has been studied by X-ray and electronic based techniques. XAS techniques generally require uranium concentrations that are too high, resulting in the observation of precipitated phases, however luminescence spectroscopy has generated several interesting observations. The basal plane was shown to give rise to little to no uranyl(VI) emission. Other studies, i.e. SHG and modelling, demonstrated the reversibility of sorption of a uranyl(VI) monovalent species, along with multiple orientations of uranyl(VI) sorption. The presence of Ca$^{2+}$ for example, limited the number of observed orientations of uranyl(VI) at the basal plane from three (without Ca$^{2+}$) to one. However, both authors concede that sorption to the edge sites are more competitive. Two major uranyl(VI) species were detected sorbed to the edge sites of muscovite. One long lived (4.0 μs) and one short lived (0.45 μs), the short lived species is red-shifted with respect to the long lived species by between 2 and 5 nm. The authors speculate about hydroxyl formation causing the observed differences, although no formal assignment is made. A red shift is usually associated with stronger equatorial bonding and a concomittent weakening of the UO$_{ax}$ bond i.e water replaced by hydroxyl, suggesting that the observed short lived species may contain a hydroxyl in addition to the bidentate bonding of the surface silanol. However, it could also equally be due to uranyl(VI) binding to an alternative surface site at a lower energy (which is probably more likely). These authors used the luminescence lifetime to define the number of water molecules in the equatorial plane, but this assignment should be taken as tentative (as discussed in Section 1.3.3). The lifetime depends on much more than the number of water molecules in the equatorial plane, namely the overall

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1 Although this study washed the samples after sorption and before measurement, which will have altered properties like the final pH, salinity and may have affected other conditions.

2 this is because the LUMO energy depends on the strength of UO$_{ax}$ bond, if elongated (from increased electron donation at the equatorial plane) the orbital rises in energy and the gap between HOMO and LUMO decreases slightly, resulting in an observed red shift.
symmetry, and rate of exchange between water molecules (determined in part by the local morphology). A recent TRLFS and PARAFAC study identified two sorption species, XOOUO$_2$ and XOOUO$_2$OH, but only when some Ca$^{2+}$ was also included, otherwise the second species was replaced with a uranyl(VI) carbonate sorption complex. They report the emission bands and lifetimes for each (Table 1-4).

Table 1-4: Luminescence emission and lifetime information for two uranyl(VI) species bound to orthoclase, from reference 145.

<table>
<thead>
<tr>
<th>Surface species</th>
<th>emission bands (nm)</th>
<th>τ (µs)</th>
<th>measurement temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;SiO$_2$UO$_2$</td>
<td>490-494; 511-515; 535-538; 561-565</td>
<td>328.28 ± 23.75</td>
<td>153</td>
</tr>
<tr>
<td>&gt;SiO$_2$UO$_2$OH</td>
<td>481; 502; 523; 546; 573</td>
<td>334.7 ± 3.1</td>
<td>153</td>
</tr>
</tbody>
</table>

1.6.5 Optical microscopy of uranyl(VI) sorption

The use of microscopy for the investigation of uranium sorption has occasionally been reported in the literature. In 2007 Grossmann et al. conducted the first investigation of uranium using confocal laser scanning microscopy (CLSM) and fluorescence spectroscopy. They were able to measure the emission of uranium particles across a microscopic image of a biofilm grown on biotite plates. Using an excitation wavelength of 408 nm, they collected a CLSM (Fig. 1-21) image which appeared to show evidence of two fluorescent precipitates, this was despite the fact that the authors geochemical modelling predicted no solid U(VI) phases. The emission spectra from the precipitates were then used to identify the oxidation state of the uranium as either U(VI) or U(V). Similar findings were made by the same authors two years later.

![Fig. 1-21: a cross section of biofilm obtained using CLSM. The authors highlight the presence of a phosphorescent uranyl(VI) species (red circle) within the autoflourescence of the biofilm. Reprinted from Grossmann et al.](image)

Around the same time, Denecke et al. published two papers using µ-XAFS, by combining the µ-XAFS data with µ-XRF data, the authors provide evidence for a U(VI) reduction mechanism via AsFeS involving the oxidation of As(0) to As(V). More
recently, Jones et al.\textsuperscript{161} used Fluorescence and Phoerphorescence Lifetime Image Mapping (FLIM and PLIM) in combination with confocal microscopy to study the bioreduction of $\text{UO}_2^{2+}$ to $\text{U(IV)}$ via \textit{Geobacter sulfurreducens}, which is known to facilitate the reduction. The authors find an emissive uranyl(VI) species bound to the surface of the \textit{Geobacter sulfurreducens} cells alongside heterogeneous extracellular mineral type features (Fig. 1-22), after several hours these are replaced by a non-fluorescent precipitate, which appeared to be $\text{U(IV)}$ in the form of uraninite. Fluorescence and phosphorescence lifetime mapping enabled the uranyl(VI) emission to be readily distinguished from the background fluorescence of the bacteria, whereas the much shorter (ns) lifetimes of uranyl(VI) associated with the bacterial cells compared to the long lived (µs lifetimes) of the extracellular features enabled the authors to visualise electron transfer processes (quenching) occurring in real time on the sub-micron scale.

\textbf{Fig. 1-22: PLIM of an extracellular feature following the introduction of urany(VI) acetate to Geobacter sulfurreducens (left) a histogram showing the distribution of resolved lifetimes for the PLIM (centre), and a representative uranyl(VI) spectrum from an extracellular feature (right) ($\lambda_{\text{ex}} = 405 \text{ nm}$, room temperature). Reprinted from Jones et al.\textsuperscript{161}}

Only one of the mentioned studies has utilised the \textit{time-resolved} emission of uranyl(VI),\textsuperscript{161} but it primarily inferred change from a reduction in intensity between measurements. The work presented in chapter 5 of this thesis is the first time the time-resolved luminescence of uranyl(VI) has been used to determine the variation in uranyl(VI) speciation across a mineral.
1.7 Project aims

The speciation of uranyl(VI) at the aqueous-mineral interface is still a rapidly growing field of research with significant implications for the disposal and remediation of uranium containing wastes and geological sites. The luminescence spectroscopy of uranyl(VI) can provide equatorial bonding information which informs the speciation in ways which other spectroscopies currently cannot. These benefits are largely owed to the relaxed constraints on experimental set up, which may also explain such significant variation in the reported luminescence properties of uranyl(VI) mineral interactions.

More advanced approaches to spectral deconvolution are gaining momentum, including the recent success of parallel factor analysis (PARAFAC) in the improved speciation of uranyl(VI) aqueous chemistry, the same methods of spectral deconvolution will be applied to excitation-emission matrices (EEM) to elucidate the speciation of uranyl(VI) bound to silica gel over a wide range of pH (3.0 – 10.0), in order to assess the suitability of the approach.

The use of modern spectroscopy (namely XAS, electronic and vibrational spectroscopies) are typically carried out on a macroscopic scale; requiring deconvolution from the signal average to reach molecular level speciation. The bulk state properties of these systems is considered a reasonable representation of the surface interactions, however this assumption may not be accurate.

This work will therefore focus on three themes and aims to:

1. Provide a reference dataset of low temperature (77 K) luminescence measurements of uranyl(VI) bound to minerals.
   a. Compare the luminescence signals to deduce surface bonding detail (speciation)
2. Use the PARAFAC algorithm to resolve the individual spectral components of uranyl(VI) excitation-emission spectra.
3. Develop a methodology for and evaluate the applicability of FLIM/PLIM measurements of uranyl(VI) at the mineral-water interface.
2 METHODS

The experimental methods, mineral characterisation techniques, spectroscopic methods and signal processing techniques are outlined in this chapter. Where suitable, references are provided with more detailed information.

2.1 Batch Sorption

All batch sorption experiments were carried out in a glove box under carbon dioxide free air. To achieve this, a Coy basic polymer glovebox was used. The glovebox was purged continuously using a pump to push air through three 500 mL Duran gas washing bottles. The bottles contained 250 mL of (in the following order) 10 M NaOH, 14 M NaOH and 17 M NaOH to remove CO₂(g). The air flow was also passed through an additional gas washing bottle containing 250 mL water in order to remove any residual NaOH aerosols.

A solution of uranyl(VI) nitrate (7.6 mg, 4x10⁻⁶ M) and NaNO₃ (4.2497 g, 0.1 M) was dissolved in degassed (using argon) and MilliQ deionised water (500 mL). 10 mL aliquots of the solution were added to centrifuge tubes (15 mL) with 0.100 g of mineral solid. Tubes were then placed on a rocking table, to ensure mixing between the solution and solid. The mixtures are then pH corrected in turn using ≤10 µL quantities of NaOH/HNO₃ (using 1 M, 0.1 M or 0.01 M, depending on the amount of acid or base required) until equilibrium had been reached. Equilibrium was reached when the pH did not drift (<0.1 change) after 12 hours. This was no shorter than two days and typically take between two and three days.

Samples were then placed in a centrifuge (10 minutes, 1400 g). The pH of the supernatant is given as the final pH value. The supernatant is then removed, the Uranium solution concentration was then determined colourimetrically after complexation with bromo-PADAP (see section 2.1.3).¹⁶²

For microscopy measurements, samples are placed on a microscope slide, whilst wet (paste like) and in the glove box, and sealed from air using a precision grade microscope coverslip (No. 1.5H), the sample is then sealed from air using two coats of hard setting polymer around the edge of the coverslip. For EEM and bulk spectroscopy
measurements, samples are added to a quartz EPR tube for low temperature measurement.

2.1.1 Approach to batch sorption
Batch sorption is used to imitate the conditions likely to result from the solvation and subsequent contact of uranium with geological materials. The technique involves the interaction of a salt solution, carrying the radionuclide of interest, with a specific mineral. The process was repeated a number of times, changing only one of the variables e.g. salinity, concentration of solute, solid to solution ratio, carbonate concentration and solid pre-treatment conditions.

**Fig. 2-1: Hierarchy overview of the experimental method 'batch sorption', as well as the intended environmental relevance and/or validation.**

An example of the batch sorption procedure, and how each step relates to the environmental conditions, is shown in Fig. 2-1, where the principle independent variable is the pH. In addition, other notable conditions, such as the total contact time,
rocking/shaking speed, temperature and total additional salinity due to pH corrections are recorded to minimise or account for the potential effect of these less sensitive but confounding variables.

The most important controlled variables to consider during the research were:

- Salinity and electrolyte composition
- Solute concentration
- Solid to solution ratio
- Carbonate concentration
- Solid pre-treatment

Salinity (0.1 M) and sodium nitrate (NaNO₃): the effect of salinity and choice of salt on the uptake and the subsequent luminescence of uranyl(VI) is noted by several authors for several different mineral systems. It was shown that an increase in the salinity generally increases the Debye length at the surface interface, which can be correlated to an increase in outer-sphere or exchange interactions. A salinity of 0.1 M was considered adequate to permit sufficient exchange interactions and applicable to most less-saline groundwater solutions. In addition, Na⁺ is the secondary counter-ion (second to the proton) common to most of the mineral systems considered and it is not as competitive with respect to cation exchange interactions as Ca²⁺. Nitrate (NO₃⁻) is frequently used because it is not a significant quencher of uranyl(VI) emission and not as reactive as other more common anions, such as sulphate, carbonate or chloride. The simplicity of the salts in the solution indicate that some value is lost with respect to the environmental relevance; however this work is interested in probing the surface interactions of uranyl(VI) with mineral interfaces following sorption, not how uranyl(VI) competes with other cations or how the intensity of luminescence is affected from alternative quenching mechanisms. Therefore, the electrolyte used throughout this research is NaNO₃.

In many contaminated lands, the concentration of uranium is low; typically 10⁻⁷ M in groundwaters and 10⁻⁵ M in mining waters. However these concentrations could not

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¹ Such as chloride, i.e. reference 46 reported a quenching rate for chloride that is 6-orders of magnitude greater than water.
always be identified by the lamp-based luminescence employed in the majority of this work. Therefore it was necessary to find a balance between an environmentally realistic and a detectable concentration of uranium. Based on preliminary experimental work a concentration of $4.0 \times 10^{-6}$ M was chosen because uranyl(VI) could be detected for all forms of measurement. Taking the solid to solution ratio into account (10 g/L) and assuming 100% uptake, the approximate parts per million (weight for weight) is $\sim 1000$ ppm.

The solid to solution ratio is most relevant when considered in tandem with the concentration of the solute and salinity. As such, the solid to solution ratio was tailored to the experimental conditions and amount of materials required for measurement and in order to minimise waste. 10 g/L was chosen as it provides an adequate amount of solid (0.1 g) for a range of measurements and 10 mL solution tubes were most suitable for fast mixing and thus quick equilibration of solutions following pH adjustment. This is an order of magnitude higher than most previous experimental work; most previous work uses lower solid to solution ratios for more convenient laboratory conditions.$^{163}$ However 10 g/L or higher more accurately reflects the environmental conditions. Some of the clay samples contain naturally high levels of Ca$^{2+}$, which is removed by pre-treating the clay with several sodium nitrate washings. This is to reduce competition with uranyl(VI) for interlayer sites.

As mentioned above, additional cations present in solution during the sorption of uranyl(VI) to the surface of minerals provides additional surface complexes thereby reducing the potential for accurate interpretation of the results. In addition, carbonate is known to heavily quench the emission of uranyl(VI).$^{118}$ All batch sorption experiments were, therefore, carried out in the absence of carbon dioxide and all solutions degassed using argon. Following batch sorption, the isolated solid is then prepared for luminescence measurement. To ensure environmental relevance, the solid is not dried or washed after batch sorption and placed immediately into the measurement vessel, either a microscope slide or EPR tube for room temperature and low temperature measurements, respectively. The samples were sealed from air and measured immediately unless otherwise stated.
Fig. 2-2: A representation of the speciation process, the recording and post-processing of uranyl(VI) luminescence data, along with justifications for each step.

The parameters selected for the recording of measurements were maintained for each mineral sample to aid comparison and are summarised in Table 2-1 and justified in Fig. 2-2. The selected parameters, such as excitation wavelength, emission wavelength, monochromator bandwidth, dwell time (continuous excitation) or gate time (pulsed excitation) and emission light filtering were fixed, following preliminary investigations and consideration of the electronic properties of uranyl(VI).

**Table 2-1: Parameters for all luminescence measurements presented in chapter 3**

<table>
<thead>
<tr>
<th>Excitation wavelength (nm)</th>
<th>Emission wavelength (nm)</th>
<th>Monochromator bandwidth (nm)</th>
<th>Dwell time (ms)</th>
<th>Gate time (ms)</th>
<th>Longpass filter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>266, 320, 405</td>
<td>520</td>
<td>± 1.5</td>
<td>0.1</td>
<td>0.1</td>
<td>455</td>
</tr>
</tbody>
</table>

### 2.1.2 Solution pH

Solution pH was measured using a Mettler Toledo LE407 Ag/Cl electrode and calibrated using a four-point standard, which was stored in 3M KCl between measurements. The electrode was fully inserted into solution and the solution was agitated until a stable reading was reached (~ 45 seconds). pH measurements are recorded to two decimal places and have an error of ± 0.1 pH unit.
2.1.3 Colourimetric analysis

Colourimetry was used to determine the concentration of uranium(VI) in the solution of the supernatant following batch sorption. The relationship is defined by the Beer-Lambert law (Eq. (16)),

\[ A = \epsilon lc \]  

(16)

where the absorbance \( (A) \) is determined by the concentration \( (c, \text{ mol L}^{-1}) \) of the absorbing compound, the extinction coefficient \( (\epsilon, \text{ L mol}^{-1} \text{ cm}^{-1}) \) and the path length \( (l, \text{ cm}) \). A linear relationship between the concentration and the absorbance is demonstrated using a series of samples with known concentrations, as demonstrated in the calibration plot (Fig. 2-3). Measurements are made using a Shimadzu UV-1800 spectrophotometer. The path length was 1 cm\(^{-1}\) and disposable polystyrene cuvettes were used for the measurements.

![Graph](attachment:image.png)

**Fig. 2-3:** Calibration plot for uranium(VI) complexation with Br-PADAP. See text for details.
2.2 Material characterisation

Several techniques are used to characterise the minerals used in this work. This includes X-ray diffraction (XRD), X-ray fluorescence (XRF) and Braunauer-Emmett-Teller (BET).

XRD uses the Bragg law to determine the spacing in crystal structures. It is extremely useful in the identification of mineral phases as many are highly crystalline, giving sharp peaks in the resulting spectra which may then be used to compare against a database of pure reference materials. XRD was carried out on a Bruker D8 and analysis carried out in EVA and peak matching was done using the International Centre of Diffraction Data (ICDD) Powder Diffraction File database.

XRF is used to determine the concentration of each metal oxide present in a mineral. The X-ray beam causes the ionisation of a core electron; the subsequent rearrangement of electrons to fill the electron hole results in the emission of line-like fluorescence, which are easily attributed to a specific element. In the identification of minerals, the technique was used to identify many of the trace metal concentrations, which are unlikely to have contributed to a significant change in the X-ray diffraction pattern. The percentages of oxides found can also be used to quantify the identification of mineral phases found in the XRD pattern. The XRF analysis was conducted using a Thermo ARL 9400 and determined the major and minor components, the analysis was carried out by Alastair Bewsher.

BET is a method of determining the specific surface area (m$^2$ g$^{-1}$) of a powdered sample. The method measures the adsorption of N$_2$ gas over a range of negative pressures at liquid nitrogen temperatures. The analysis was conducted using a Micrometrics Gemini V BET surface area analyser.

Two montmorillonites (STx-1b and SWy-2) and one kaolinite (KGa-1b) used in this study have been sourced from the clay minerals society (see Table 2-2), characterisation of the source clays is well detailed.$^{164}$ However, additional XRD patterns, surface area (via BET measurement), and in some cases XRF (Fig. 2-4), have been collected to characterise the minerals used and have been summarised in Table 2-3.
Table 2-2: Properties of sourced clay minerals. See text for source.

<table>
<thead>
<tr>
<th>Mineral code</th>
<th>Mineral type</th>
<th>Origin</th>
<th>Surface area (m²/g)</th>
<th>Cation Exchange Capacity (meq/100 g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWy-2</td>
<td>Na-Montmorillonite</td>
<td>Wyoming; Newcastle formation (cretaceous)</td>
<td>31.82 ± 0.22</td>
<td>76.4</td>
</tr>
<tr>
<td>STx-1b</td>
<td>Ca-Montmorillonite</td>
<td>Texas; Manning formation, Jackson group (eocene)</td>
<td>83.79 ± 0.22</td>
<td>84.4</td>
</tr>
<tr>
<td>KGa-1b</td>
<td>Kaolinite (low defect)</td>
<td>Washington, Georgia, USA</td>
<td>10.05 ± 0.22</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Table 2-3: Table listing the percentage by weight of each metal in the two montmorillonite clays considered in this study. Results listed are from XRF measurement. CEC (cation exchange capacity) is reported from ref¹⁶⁴.

<table>
<thead>
<tr>
<th>% composition</th>
<th>Stx-1b</th>
<th>Swy-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>70.1</td>
<td>62.9</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>16.0</td>
<td>19.6</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.22</td>
<td>0.090</td>
</tr>
<tr>
<td>Fe₂O₃ &amp; FeO</td>
<td>0.80</td>
<td>3.67</td>
</tr>
<tr>
<td>MnO</td>
<td>0.009</td>
<td>0.006</td>
</tr>
<tr>
<td>MgO</td>
<td>3.69</td>
<td>3.05</td>
</tr>
<tr>
<td>CaO</td>
<td>1.59</td>
<td>1.68</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.27</td>
<td>1.53</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.078</td>
<td>0.53</td>
</tr>
<tr>
<td>F</td>
<td>0.084</td>
<td>0.111</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.026</td>
<td>0.049</td>
</tr>
<tr>
<td>S &amp; SO₃</td>
<td>0.04</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Property

<table>
<thead>
<tr>
<th>Property</th>
<th>Stx-1b</th>
<th>Swy-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEC</td>
<td>84.4 meq/100g</td>
<td>76.4 meq/100g</td>
</tr>
<tr>
<td>BET</td>
<td>83.79 m²/g</td>
<td>31.82 m²/g</td>
</tr>
</tbody>
</table>
Fig. 2-4: A plot of the relative metal oxide concentrations for the minor metal components are presented side by side to expose differences.

### 2.2.1 XRD patterns

As the most effective way of confirming a mineral phase, the XRD patterns of the minerals intended for study were collected. A summary of the phases identified in the patterns are shown in Table 2-4, full XRD spectra are included in the Appendix.

Table 2-4: A summary of the phases identified for each of the minerals being investigated based off of assignment of their XRD patterns. Full patterns available in the Appendix.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Mineral Phases identified</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite</td>
<td>Kaolinite only</td>
</tr>
<tr>
<td>Montmorillonite Stx-1b</td>
<td>Na-Montmorillonite, Opal-CT.</td>
</tr>
<tr>
<td>Silica gel</td>
<td>Amorphous phase only</td>
</tr>
<tr>
<td>Montmorillonite Swy-1</td>
<td>Montmorillonite; Quartz; Biotite; Anorthite</td>
</tr>
<tr>
<td>Boehmite</td>
<td>Boehmite only</td>
</tr>
<tr>
<td>Bayerite</td>
<td>Bayerite only</td>
</tr>
</tbody>
</table>

### 2.3 Bulk Luminescence

Bulk luminescence is the term used to describe the collection of luminescence from an instrument which disregards temporal effects, in other words the measurement considers the average signal over a macroscopic area of material. It is required in order to differentiate it from microscopic luminescence.
Bulk luminescence measurements are made using an Edinburgh Instruments FLSP920 Fluorescence Spectrometer, the instrument includes all of the hardware and software required for recording steady-state and time-resolved luminescence.

A light source is required to induce luminescence in a sample. The instrument is fitted with two primary light sources. The first is the continuous Xenon lamp (Xe900), used in this work for the acquisition of steady state emission spectra in compiling excitation-emission matrices and excitation or emission spectra. The second is the Microsecond flashlamp (μF920H), which is used to acquire time-resolved measurements in the microsecond to second range. The Xe900 and μF920H power profiles are given in Fig. 2-5. Correction files account for changes in the power output of the light sources. Also note the highest energy with an appreciable power output for the Xe900 is at 255 nm (10 a.u.)

![Fig. 2-5: Left, spectral output profile for Xe900 in relative power units. Right, spectral output profile for μF920H in relative power units. From FLSP920 Series User Guide.](chart)

The arc of light from the bulb of the light source is focused onto an excitation monochromator via a mirror and an adjustable lens assembly. A monochromator transmits a narrow band of light from the broad spectrum of the light source, the spectrometer has two monochromators, one for the selection of excitation light and a second for the selection of emission light. Monochromators work by focusing the light onto a series of mirrors, one of which is the grating turret; an adjustable mirror, which focuses only those wavelengths required by the user, discarding the rest. A simple schematic is presented in Fig. 2-6. Two entrances are required for the two primary light sources, controlled by the shutter swing mirror.
Fig. 2-6: Schematic of single-grating excitation monochromator, from FLSP920 Series User Guide. Note the Emission monochromator works in reverse.

Light leaves the monochromator and is focused, using a lens, towards the sample holder, 7 cm away. If the monochromater is set to a band pass of 1 nm, the beam will be 0.24 mm wide at the sample position. The emission is collected at 90° to the incident excitation light. There are two sample holders used in this work: the first and most relevant to EEMs is the quartz EPR Dewar, designed to hold a liquid nitrogen bath and sample contained in an EPR tube. The sample is thus cooled to 77 K. The second is the microscope slide holder, samples intended for microscope measurement may also be measured by the luminescence spectrometer to check the photoluminescence response. Sample holders are fixed to the base of the instrument, ensuring the alignment of the excitation/emission path.

A long-pass filter is used to remove light of higher energy than the emission measurement range, which includes excitation light, and therefore minimises higher order effects. Higher order effects arise when the monochromator permits light of half, a third, a fourth and so on, of the selected monochromator value, resulting in a spike in the observed emission at these frequencies. For EEM measurements, the 455 nm long pass filter is used, it is able to filter out all the excitation light over the excitation energy range, and is close to the highest energy emissive light (≈480 nm). Additionally, no higher order effects, owed to the emission, should be observed based within the emission range.
considered (480 nm – 600 nm). After passing through the emission monochromator, light is recorded using a single photon counting photon multiplier tube (PMT) detector. The lifetime data collected for chapter 3 is of samples measured at 77K over 2 ms with 4000 time channels, thus channel bins are in 0.5 µs steps.

2.4 Microscopic Luminescence (FLIM/PLIM measurements)
The luminescence maps presented in chapter 5 are combined fluorescence/phosphorescence confocal lifetime image maps (FLIM/PLIM) acquired using a commercial system from Becker and Hickl with a modulated diode laser (405 nm). Emission light is focused through a x60 water immersion objective with a natural aperture (NA) of 1.2 on an inverted Nikon microscope (Ti-E). Light is collected without de-scanning, therefore by-passing the scanning system, and is then directed through a long-pass filter (475 nm, BG39, Comar). The images are enhanced by an optical zooming factor of 3.05 to obtain a viewing window of 92 by 92 µm, or ~0.36 µm per pixel. The scan was operated in the normal mode and line, frame and pixel clock signals were generated and synchronized with an external fast micro-channel plate photomultiplier tube (Hamamatsu R3809U) used as the detector. These were linked via a time-correlated single photon counting (TCSPC) PC module SPC1500 (Becker and Hickl). This configuration of equipment provided instrument quantum efficiencies of more than 30% with single photon detection capabilities. Steady state spectra were recorded using an Ocean Optics USB2000+ spectrometer.

The collection time for each measurement was fixed to ten minutes with the excitation laser power set to 90%, which was deemed adequate to collect enough photons to fit the lifetime image maps.

2.5 Raman microscopy
All Raman measurements were made using a Horiba Scientific XploRA Plus Confocal Raman Microscope using a 638 nm laser source and analysed using Labspec 6 Raman Software Suite.

The scan used in section 5.3.5 is comprised of 1120 (35 by 32) spot scans across the sample, and the space between adjacent scans was approximately 2.3 µm. Each spot scan is an average of three 15 second scans. It took approximately 15 hours to complete. The
peak comparisons were made using OriginPro 8, silica gel was identified by a shift at 491.746 cm\(^{-1}\) and bayerite by a strong shift at 545.174 cm\(^{-1}\).

### 2.6 Signal Processing

Signal processing was carried out using OriginPro 8 and/or Matlab 2017a. Signal processing simply refers to all of the post-processing involved in the analysis of the collected luminescence data. Firstly, the spectra are corrected using the spectrometer correction files and in the case of 3-way EEMs, scaled in the emission mode.\(^1\) Secondly, 2-way data is immediately analysed using a series of derivative methods to determine the peak positions. This involves ‘signal enhancement’ (defined below), the third derivative (also defined below) with a degree of smoothing (neighbour point-averaging); smoothing is required since each derivative approximately squares the noise. In many cases, it was not possible to fit the emission data further by modelling to pseudo-Voigt curves as originally intended. 3-way data requires a form of analysis that can simultaneously consider the 3 dimensions, hence the analysis require non-classical methods, which are given more explanation in chapter 4. Parallel factor analysis (described in section 4.1.1) was implemented, the outputs of which were then fit to pseudo-Voigt (90% Lorentzian) curves. The distance between successive curves was constrained such that the vibrational separation was equal to or less than the previous separation (a condition of the Morse potential, see section 1.2.1).

The derivative method ‘signal enhancement’ employs the second and fourth derivative to more easily expose the signal maxima of a complex signal, as in Equation (17):

\[
ES = S - k_2S'' + k_4S''''
\]  

(17)

where ES is the enhanced signal, S is the original signal, \(k_2\) and \(k_4\) are weighting factors for the second and forth derivatives respectively, \(S''\) is the second derivative and \(S''''\) is the fourth derivative.

The effect is demonstrated in Fig. 2-7. The third derivative of a curve can be used to find the approximate positions of peaks. By solving for values at \(y=0\), this way all points at which the direction of the gradient is inverted are identified. After each derivative, any

\(^{1}\) For more information of pre-processing of data matrices for multi-way analysis see reference 177
noise in the curve is squared, smoothing before calculating each derivative is usually required to obtain a reasonable third derivative function.

Fig. 2-7: Two emission spectrum signals are shown that contain two underlying overlapping signals. The spectra are sharpened using signal enhancement. The peak maxima are now easily resolved.

It should be noted that this methodology is not intended to extract the absolute shape of the underlying peaks (note the negativity in intensity between peaks, especially for component 2, Fig. 2-7) but to enhance the identification of the central maximum of the underlying peaks.

Lifetime data are fit by an exponential decay model in OriginPro 8 using the built in exponential decay function ‘ExpDec1’ equation (18) which includes a y-offset term, $y_0$.

$$y = y_0 + Ae^{-x/\tau}$$

(18)

No bounds are placed on the offset, amplitude (A) or decay constant ($\tau$) terms. Each curve is initially fit to a single exponential decay, which increases if the shape of the residual does not tend to a value of zero, i.e. the residual contains a non-linear (specifically, non $y=0$) shape, up to a total of three exponential decay terms. The fitting
of phosphorescent lifetime maps was conducted with a manually determined y-offset as defined within section 5.2.
3 URANYL(VI) SORBED TO MINERALS: A COMPREHENSIVE LUMINESCENCE DATASET

3.1 Introduction

This chapter provides a detailed account of the excitation, emission and lifetime properties for uranyl(VI) sorbed to silica gel and quartz; bayerite and boehmite; muscovite and kaolinite; and STx-1b and SWy-2 montmorillonite, all measured at 77K. These measurements are used to assess the extent to which the luminescent properties of uranyl(VI) are able to describe the molecular interactions at the mineral-water interface. All of the assignments are placed into the context of the available literature, which has been discussed at length in chapter 1. Certain aspects of uranyl(VI) luminescence are more comparable than others. For example, luminescence emission intensity is variable and dependent on instrumentation or sample preparation, and the reproducibility of a single emissive species peak positions has been shown to vary by between 0.6 and 2.0 nm, depending on the peak being examined. The luminescence lifetime is also particularly sensitive to temperature. Thus cross-literature examination is only useful for comparing trends in data and not absolute values. Only luminescence measurements made under well controlled identical conditions (i.e. with the same equipment and researcher) are comparable in a quantitative way. These requirements are born out in this assessment.

The results of the analysis of uranyl(VI) emission spectra are quantified by peak positions. Each identified unique set of uranyl(VI) luminescence emission peaks are grouped into a unique overall signal which therefore represent a species. A species is then represented by an arbitrary code, made using the relevant mineral followed by a letter starting from A. For example, the first species identified on quartz is given the species code QuaA. The three letter code given to represent each of the minerals is defined unambiguously in the table caption of Table 3-1.

3.2 Methods and presentation of results

All of the luminescence measurements in this chapter were conducted at a temperature of 77K and recorded using a simple fluorimeter set up, which is outlined in detail in the methods (section 2.3). The excitation spectrum of each sample is recorded over the range 250 nm to 450 nm using an excitation monochromator bandwidth of 1.5 nm, the
recorded spectrum is defined as the change in intensity of emission recorded at 520 ± 10 nm. Due to the range of possible excitation pathways detailed in section 1.3, three separate emission spectra are measured. The emission spectra are recorded over the range 460 to 600 nm with a bandwidth of ± 1.5 nm. These are collected using different excitation energies, which are 266 nm, 320 nm and 405 nm, with an excitation bandwidth of ± 10 nm for each measurement. The three excitation wavelengths are chosen to best represent the variable excitation energies reported in the literature. These measurements are steady state measurements, meaning they are not time-resolved. For time-resolved measurements, a microsecond lamp was used (see Section 2.3 for full details). These were also recorded at excitation energies of 266 nm, 320 nm, and 405 nm, whilst the emission wavelength was always 520 nm with a bandwidth on both the excitation and emission monochromator of ± 1.5 nm. Due to the sheer magnitude of data this method produced, the emission and excitation spectra are compiled into stacks, and luminescence lifetimes are tabulated separately in the Appendix, and only stated within the text when necessary.

Emission spectra are processed using a derivative-based approach outlined in Section 2.6. The algorithm takes the raw emission response and outputs the underlying peak positions; these peak positions are then compiled into a list and assigned to species based on a visual comparison to the ‘signal enhanced’ spectra (calculation details are presented in Section 2.6) and must also have reasonable vibrational spacings (700 < ν1 < 900, within error). Each of these ‘species’ are then compiled according to excitation wavelength (266, 320 or 405 nm), pH (4, 6, 8 or 10) and the mineral to which uranyl(VI) is sorbed. Once the process is complete comparisons between like spectra are drawn for samples of the same mineral system but of different excitation energy and/or pH. These averaged peak values are tabulated and the vibrational spacing calculated as the difference between the 1st and 2nd peak (peaks are ordered from highest energy to lowest energy) as well as the difference between the 2nd and 3rd peak (because the error on the 1st peak is often larger (it is less intense) than for the 2nd and 3rd peaks this spacing has a lower associated error). Each one of these is then assigned as a single species, for example QuaA (using the code outlined above). The excitation spectra are not post-processed and are used to guide the speciation of the identified emissive species. The lifetime measurements are all fit
according to the most suitable exponential decay function (this is determined by a consideration of the $\chi^2$ and the shape of the residual) and also used to guide the speciation of the identified emissive species.

The results are presented in the following format: firstly the key findings are summarised, then the results table for the identified species including errors, followed by the compiled emission and excitation spectra. Finally, this is followed by an explanation and discussion of the key findings in the context of the available literature.

3.3 Results

3.3.1 Batch sorption

Batch sorption was carried out in the absence of carbonate, a solid to liquid ratio of 10 g/L and using a simulated groundwater solution including UO$_2^{2+}$ (4x10$^{-6}$ M, 10 mL) as described in section 2.1. The final pH values for each mineral are listed in Table 3-1 and sorption profiles are presented in Fig. 3-1. From these results, it is clear that sorption for the minerals are broadly similar except for quartz, which is most likely saturated owed to its large particle size and therefore low surface area. All of the other minerals are under-saturated, demonstrated by the observation of near 100% sorption at pH 6, 8 and 10. The sorption data are comparable to literature (SWy,$^{32}$ KGa,$^{136}$ STx,$^{136}$ muscovite,$^{156}$ silica,$^{114}$ quartz,$^{124}$ bayerite$^{103}$).

Table 3-1: Final pH values following batch sorption of uranyl(VI). Mineral samples are represented by a three letter code as follows. SIL: Silica gel; BOE: Boehmite; BAY: Bayerite; STX: Montmorillonite (Na-STx-1b); SWY: Montmorillonite (SWy-2); MUS: Muscovite; KAO: Kaolinite; QUA: Quartz. No error is reported but a standard deviation of 0.1 pH unit is recommended, as outlined in 2.1.2.
3.3.2 The luminescence of uranyl(VI) bound to bayerite and boehmite

Bayerite and boehmite are the two aluminium phases studied. They are intended to represent a range of aluminium hydroxide and aluminium oxyhydroxide interactions. As highlighted in the literature review of uranyl(VI) interactions with these minerals (section 1.4.1), several interactions with aluminol sites are possible and that is demonstrated by the main findings of this work.

Only two uranyl(VI) luminescence species are detected over the full pH range (4, 6, 8 and 10) bound to bayerite, labelled BayA and BayB, and both the excitation and emission spectra are independent of pH. The 2nd vibrational stretching frequencies for the two species are $838.2 \pm 11.0$ cm$^{-1}$ and $786.4 \pm 10.7$ cm$^{-1}$, respectively. The identification for two separate species is further supported by lifetime data, which was modelled to a bi-exponential decay and also appears independent of pH. However, a third bayerite species may be present at pH 4, but its signal is too weak to resolve. Three uranyl(VI) species are resolved via emission spectra sorbed to boehmite over the four samples at pH 4, pH 6, pH 8 and pH 10; BoeB is resolved at all pH values studied; BoeA resolved at pH 4.
and pH 6 only; BoeC resolved at pH 8 and pH 10 only. Very little or no correlation can be drawn between the species bound to bayerite and the species bound to boehmite.

**Table 3-2: Summary of emission parameters determined from low temperature (77K) emission measurements at excitation wavelengths 266 nm, 320 nm and 405 nm for uranyl(VI) sorbed to bayerite (Bay) and boehmite (Boe).**

<table>
<thead>
<tr>
<th>Comment</th>
<th>In all</th>
<th>In all</th>
<th>In pH 4 and 6</th>
<th>In all</th>
<th>In pH 8 and 10</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Species</strong></td>
<td>BayA</td>
<td>BayB</td>
<td>BoeA</td>
<td>BoeB</td>
<td>BoeC</td>
</tr>
<tr>
<td>1st peak (nm)</td>
<td>478.58</td>
<td>483.45</td>
<td>479.86</td>
<td>485.06</td>
<td>477.14</td>
</tr>
<tr>
<td>Error</td>
<td>4.77</td>
<td>0.60</td>
<td>0.99</td>
<td>1.07</td>
<td>0.91</td>
</tr>
<tr>
<td>2nd peak (nm)</td>
<td>492.93</td>
<td>500.77</td>
<td>497.84</td>
<td>505.12</td>
<td>495.17</td>
</tr>
<tr>
<td>Error</td>
<td>0.49</td>
<td>0.96</td>
<td>1.61</td>
<td>0.76</td>
<td>0.58</td>
</tr>
<tr>
<td>3rd peak (nm)</td>
<td>514.17</td>
<td>520.71</td>
<td>523.32</td>
<td>525.86</td>
<td>517.46</td>
</tr>
<tr>
<td>Error</td>
<td>0.54</td>
<td>1.01</td>
<td>0.60</td>
<td>2.09</td>
<td>0.33</td>
</tr>
<tr>
<td>1st space (cm⁻¹)</td>
<td>618.75</td>
<td>707.92</td>
<td>752.88</td>
<td>818.75</td>
<td>763.08</td>
</tr>
<tr>
<td>Error</td>
<td>166.23</td>
<td>61.31</td>
<td>22.21</td>
<td>75.05</td>
<td>16.13</td>
</tr>
<tr>
<td>2nd space (cm⁻¹)</td>
<td>838.23</td>
<td>786.36</td>
<td>983.07</td>
<td>801.69</td>
<td>869.98</td>
</tr>
<tr>
<td>Error</td>
<td>10.98</td>
<td>10.75</td>
<td>113.31</td>
<td>112.54</td>
<td>11.46</td>
</tr>
<tr>
<td>1st peak (cm⁻¹)</td>
<td>20895</td>
<td>20685</td>
<td>20840</td>
<td>20616</td>
<td>20958</td>
</tr>
</tbody>
</table>
Fig. 3-2: Emission spectra for the boehmite (BOE) and bayerite (BAY) sample series at specified pH values. Spectra are separated by excitation energy and stacked with a slight offset to aid comparison and minimise overlap.
Fig. 3-3: Excitation spectra for the boehmite (BOE) and bayerite (BAY) sample series at specified pH values. Spectra are stacked with a slight y-axis offset to aid comparison and minimise overlap. See key in Fig. 3-2 for spectra identification.

The two major emissive species that are present across the pH range 4 to 10 bound to bayerite, have peak centres as shown in Table 3-2. It’s highly likely that these species co-exist and are of similar energies, making their formation on the bayerite surface equally likely. Both are most likely inner-sphere complexes forming at edge-sites. Where they differ, however, is likely in the positioning at the edge site. Hattori et al. used DFT and EXAFS to observe uranyl(VI) complexes adsorbed to the edge site of gibbsite and defined two likely and energetically similar complexes, edge-sharing and corner-sharing. In their study, the corner sharing complex had an oxygen atom from the aluminium oxide that is within 3 Å of the uranium atom. This difference could be sufficient to result in the differences in the observed emission spectrum (Fig. 3-4) and vibrational properties (Table 3-2), and the biexponential decay of the emission (short component is 50-150 µs and long component is 270-380 µs, range is large due to dependency on excitation energy). The unresolved third component at pH 4 may refer to a hydrated uranyl(VI) species that is only very weakly associated with the bayerite.

---

1 Bayerite edge-sites would produce similar results, since these calculations consider the edge of a single sheet, and the difference between bayerite and gibbsite is only in the orientation of adjacent sheets (see chapter 1.4.1)
The observation of three distinct emissive species sorbed to boehmite shows that a transition occurs between pH 6 and pH 8 where BoeA blue-shifts by ~2 nm to a slightly higher energy and labelled as BoeC (Fig. 3-2). The uranyl(VI)-boehmite sorption system has rarely been reported in the literature and speciation detail is much more speculative than for bayerite. However, the orthorhombic structure of boehmite represents significantly higher symmetry than the monoclinic bayerite. One possible cut showing the edge and surface of boehmite is shown in Fig. 3-5. Both the ‘edge’ and ‘surface’ present reasonable equatorial bonding environments for uranyl(VI). Finally, the OH groups indicated by the solid arrows in Fig. 3-5 are likely protonated at pH 6 or below and deprotonated at pH 8 or above. It follows that uranyl(VI) bound to the surface is likely represented by BoeA at and below pH 6 and BoeC at or above pH 8. The edge

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1 It appears unlikely that a corner-sharing motif like that seen for bayerite would be viable for boehmite due to the much poorer steric, although this analysis would require computational modelling, preferably where the surface is allowed to relax from its crystal structure.
site, which would be less significantly affected by pH within the range pH 4 – pH 10, would then provide an unchanging bonding environment for uranyl(VI) represented by BoeB.

![Boehmite structure showing the edge (dotted arrow), interlayer (dashed arrow) and surface (solid arrow). Water molecules line up around the exposed Al atoms at the edge (not drawn), Sheets are held together by hydrogen bonding at the interlayer. Uranyl(VI) is most likely to interact with the edge and surface sites.](image)

The diversity of aluminium hydroxide/oxides and the resulting diversity of uranyl(VI) luminescence upon sorption confirms the complexity that should be expected by the identification of uranyl(VI) sorption to heterogeneous aluminium rich sediments. The lifetime data somewhat supports the observation that BoeA is replaced by BoeC as pH is increased between pH 6 and pH 8. This is evidenced by the observation of similar lifetime properties for the pH 4 and 6 samples (i.e. $\tau_2 = 700 \mu$s at $\lambda_{ex} = 266$ nm), and that a change occurs at and above pH 8 (i.e. $\tau_2 = 800 \mu$s at $\lambda_{ex} = 266$ nm). In addition, it would appear that the lifetime of BoeC has a pH dependency (dropping to 350 $\mu$s at pH 10),

---

1. Outside of this range, it’s very likely that boehmite would begin to dissolve.
suggestion that it may undergo some more minor environmental change as pH is increased from pH 8 to pH 10.

3.3.3 The luminescence of uranyl(VI) bound to quartz and silica gel

Silica gel and quartz are the two silicon oxide phases chosen in this study. As highlighted in section 1.4.2, quartz is crystalline and silica gel is amorphous. This is expected to result in significant differences in the nature of the bonding of uranyl(VI) to the surface of the mineral as either a monodentate species (quartz) or bidentate species (silica gel), as determined from the literature (see section 1.6.2). Analysis of the emission (Fig. 3-6) and excitation (Fig. 3-7) spectra afford the following key findings.

The emission of uranyl(VI) sorbed to quartz is dominated by a single emissive species, labelled QuaA. This species is present irrespective of pH (Table 3-3), and most clearly resolved following excitation at 266 nm. QuaA is very likely $\text{[SiO}_2\text{UO}_2\text{OH}]$. Two additional species are resolved, one at pH 6 (QuaB) and a second at pH 8 (QuaC). Both are most clearly resolved following 320 nm excitation and give rise to the large deviations in excitation spectra for the pH 6 and pH 8 samples. These have not previously been observed and identification is speculative. A fourth emission species with a very broad emission spectrum is observed at pH 10, which is most likely soddytite.

The emission of uranyl(VI) sorbed to silica gel results in two emissive species which are dependent on pH. In general, an increase in excitation energy is correlated with a red shift in the emission spectrum and a decrease in the observed lifetime of a single species.

Table 3-3: Summary of emission parameters determined from low temperature emission measurements at excitation wavelengths 266 nm, 320 nm and 405 nm for uranyl(VI) sorbed to silica gel and quartz.

<table>
<thead>
<tr>
<th>comment</th>
<th>low pH</th>
<th>high pH</th>
<th>in all</th>
<th>pH 6 only</th>
<th>pH 8 only</th>
</tr>
</thead>
<tbody>
<tr>
<td>species</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1st peak (nm)</td>
<td>SIIA</td>
<td>SIIB</td>
<td>QuaA</td>
<td>QuaB</td>
<td>QuaC</td>
</tr>
<tr>
<td>error</td>
<td>494.75</td>
<td>501.98</td>
<td>479.34</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>2nd peak (nm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>error</td>
<td>0.76</td>
<td>0.74</td>
<td>0.64</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>3rd peak (nm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>error</td>
<td>516.00</td>
<td>523.18</td>
<td>499.18</td>
<td>506.82</td>
<td>516.22</td>
</tr>
<tr>
<td>1st space (cm$^{-1}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>error</td>
<td>832.33</td>
<td>807.33</td>
<td>822.18</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>2nd space (cm(^{-1}))</td>
<td>824.06</td>
<td>808.27</td>
<td>786.24</td>
<td>823.01</td>
<td>822.15</td>
</tr>
<tr>
<td>-------------------------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
</tr>
<tr>
<td>error</td>
<td>30.38</td>
<td>12.98</td>
<td>20.64</td>
<td>2.60</td>
<td>N/A</td>
</tr>
<tr>
<td>1st peak (cm(^{-1}))</td>
<td>20212</td>
<td>19921</td>
<td>20862</td>
<td>N/A</td>
<td>20293</td>
</tr>
</tbody>
</table>

Fig. 3-6: Emission spectra for the quartz (QUA) and silica gel (SIL) sample series at specified pH values. Spectra are separated by excitation energy and stacked with a slight offset to aid comparison and minimise overlap.
The most dominant emissive species, QuaA, is comparable to previously reported emissive species for uranyl(VI) bound to quartz. The complex has a very high energy first peak (20,862 cm\(^{-1}\)), lower even than the first peak of uranyl(VI) in aqueous solution (20,510 cm\(^{-1}\)). These sorts of blue shifts are commonly observed for bidentate complexes such as uranyl(VI) carbonate or uranyl(VI) phosphate. Thus, the binding site involved will most likely also be from a bidentate group, such as >SiO\(_2\) (see Fig. 3-8). The uranyl(VI) is present at every pH, which raises the question of whether or not it contains a hydroxyl group. By considering the aqueous chemistry, it might be expected that the complex contains a single hydroxyl, and such an assignment has been made by previous authors who reported very similar emission spectra.

The two minor uranyl(VI) species bound to quartz are poorly resolved and in some cases it has not been possible to reliably determine the peak positions. These species are left undefined at this stage, but the relationship between 320 nm and selective excitation of minor species is noted as a key observation, as this likely indicates the availability of a ligand excitation pathway that was not available to the QuaA complex. Finally, an extremely broad emissive species between 520 and 600 nm is observed in the pH 10
sample, which may represent a uranyl(VI)-silicate precipitate, although cryogenic measurements would be required to clarify its exact nature. The experimental conditions used here would suggest the phase is soddyite \( [(\text{UO}_2)_2\text{SiO}_4](\text{H}_2\text{O})_2 \).

Analysis of the silica gel emission spectra confirms the commonly reported trend in uranyl(VI) sorbed to silica gel with increasing pH, as observed by several authors. In this work the red shift is approximately 7 nm, which is comparable to the cited literature. The peak positions and vibrational spacings are reported in Table 3-3 for the two complexes. Complex SilA (dominant at lower pH) is more weakly coordinated to the silica surface than SilB (dominant at higher pH), as noted by the higher energy first peak, indicating less electron donation from equatorial bonding. Many authors have postulated the speciation of these two species, which is discussed at length in the literature review (1.6.2). The main difference that causes the significant red shift compared to QuaA is that the surface is bidentate, not monodentate, (i.e. \((\text{SiO})_2\), not \(\text{SiO}_2\)), and that the red-shift at higher pH is due to hydrolysis of \(\text{UO}_2\) to \(\text{UO}_2\text{OH}\), hence SilA represents \(>(\text{SiO})_2\text{UO}_2\) and SilB represents \(>(\text{SiO})_2\text{UO}_2\text{OH}\).

It would appear that with an increase in the excitation energy, both the absolute position of the peaks in the observed emission and the observed lifetime are consistently affected towards a system that represents a measurement at a higher temperature. During the excitation emission process, energy is dissipated by vibrations (i.e. heat); this is particularly true for excitation at higher energies, which must go through more energy transfer and relaxation pathways.

Some other observations which are notable include the fact that uranyl(VI) sorbed to silica gel gives rise to the most intense emission of all the samples considered in this study. This property of silica gel is well documented, and is likely due to inhibited collisional quenching and water exchange within the pores of the amorphous silica gel compared to the mostly crystalline ‘exposed’ sorption of uranyl(VI) to the other, more crystalline minerals.

---

1 Although not explored in this work, Wang et al. provide evidence that increasing the contact time has a similar effect to increasing the pH.
Room temperature measurements produce luminescence excitation and emission spectra that contain the same fundamental electronic and vibrational information (i.e. peak maxima) but have much poorer signal to noise ratios. All measurements that do not contain some form of amorphous silica do not produce readable luminescence properties at room temperature using the experimental set-up in this work. Clearly, the luminescence enhancing property of amorphous (silica) phases outlined previously permits good signal to noise ratios that provide discernible signals for room temperature measurements. However, any other more crystalline phase gives rise to a uranyl(VI) species that is too heavily quenched and therefore too poorly resolved. For this reason, all of the measurements presented here are at low temperature (77 K).

Excitation spectra at energy higher than the fingerprint region (~420 nm) results in banding dependent on the pH. A band is a range of energies that can be used to excite a local orbital and result in the observation of uranyl(VI) emission. The bands themselves contain vibrational character and represent the vibrational spacing of the excited state. Bands become accessible or inaccessible depending on the speciation, as observed by changes in the excitation spectra, and thus could be used to infer the presence or absence of a particular energy transfer pathway and hence, equatorial ligand.\(^1\) Such character may provide information into the speciation of the silica gel and quartz samples. The availability, or lack thereof, of an excitation band provides insight into the modes of excitation which depend on changes in the equatorial bonding, and thus the speciation. These bands are the subject of discussion in chapter 4.

---

\(^1\) It should be noted at this point that many of the vibrational spacings of excited states are not considered particularly useful as theoretical computational work is generally unable to accurately calculate them and there are few alternative experimental setups that can observe them.
3.3.4 The luminescence of uranyl(VI) bound to montmorillonite (STx-1b and SWy-2 sourced clays)

Having examined the emission spectra and decay constants (lifetimes) of uranyl sorbed to the single mineral systems that are the major constituents of montmorillonites, this data was used for comparison with the emission profiles of uranyl sorbed to montmorillonite and to identify common sorption species. The two montmorillonite samples SWy-2 and STx-1b differ most significantly by their inclusion of semi-crystalline opal-CT (STx-1b has ~30% opal CT, SWy-2 has <1%) whereas the more commonly reported reason for their difference is their iron concentrations (STx-1b is 0.8% and SWy-2 is 3.67%). The results of the emission (Fig. 3-9) and excitation (Fig. 3-10) data produced here display considerable differences in the speciation.

Uranyl(VI) sorbed to SWy is characterised by three distinct emissive species; at pH 4 only one species is resolved. This species is replaced at pH 6, 8 and 10 by two additional emissive species. By contrast, uranyl(VI) sorbed to STx clay is characterised by four distinct emissive species. The assignment of these emissive species is complex with considerable dependency on excitation wavelength.

Table 3-4: Summary of emission parameters determined from low temperature (77K) emission measurements at excitation wavelengths 266 nm, 320 nm and 405 nm for uranyl(VI) sorbed to montmorillonites STx-1b (STX) and SWy-2 (SWY).

<table>
<thead>
<tr>
<th>comment</th>
<th>in all</th>
<th>in 4, 6 and 8</th>
<th>in pH 4 only</th>
<th>in pH 6, 8 and 10 only</th>
</tr>
</thead>
<tbody>
<tr>
<td>species</td>
<td>STxA</td>
<td>STxB</td>
<td>STxC</td>
<td>STxD</td>
</tr>
<tr>
<td>1st peak (nm)</td>
<td>493.68</td>
<td>498.51</td>
<td>481.99</td>
<td>506.32</td>
</tr>
<tr>
<td>Error</td>
<td>1.85</td>
<td>0.81</td>
<td>0.95</td>
<td>0.29</td>
</tr>
<tr>
<td>2nd peak</td>
<td>513.96</td>
<td>518.71</td>
<td>502.08</td>
<td>528.74</td>
</tr>
<tr>
<td>Error</td>
<td>1.85</td>
<td>1.18</td>
<td>0.66</td>
<td>0.36</td>
</tr>
<tr>
<td>3rd peak</td>
<td>537.13</td>
<td>541.92</td>
<td>523.29</td>
<td>550.76</td>
</tr>
<tr>
<td>Error</td>
<td>4.09</td>
<td>1.07</td>
<td>0.67</td>
<td>2.90</td>
</tr>
<tr>
<td>1st space (cm$^{-1}$)</td>
<td>827.69</td>
<td>814.25</td>
<td>830.18</td>
<td>837.12</td>
</tr>
<tr>
<td>Error</td>
<td>49.02</td>
<td>28.64</td>
<td>48.48</td>
<td>14.14</td>
</tr>
<tr>
<td>2nd space</td>
<td>841.12</td>
<td>814.66</td>
<td>807.50</td>
<td>755.96</td>
</tr>
<tr>
<td>Error</td>
<td>132.29</td>
<td>56.65</td>
<td>1.77</td>
<td>86.03</td>
</tr>
<tr>
<td>1st peak (cm$^{-1}$)</td>
<td>20256</td>
<td>20060</td>
<td>20747</td>
<td>19750</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>comment</th>
<th>in all</th>
<th>in 4, 6 and 8</th>
<th>in pH 4 only</th>
<th>in pH 6, 8 and 10 only</th>
</tr>
</thead>
<tbody>
<tr>
<td>species</td>
<td>SWyA</td>
<td>SWyB</td>
<td>SWyC</td>
<td></td>
</tr>
<tr>
<td>1st peak (nm)</td>
<td>502.28</td>
<td>500.32</td>
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</tr>
<tr>
<td>Error</td>
<td>1.21</td>
<td>1.49</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>2nd peak</td>
<td>523.29</td>
<td>520.67</td>
<td>513.48</td>
<td></td>
</tr>
<tr>
<td>Error</td>
<td>0.05</td>
<td>1.32</td>
<td>1.22</td>
<td></td>
</tr>
<tr>
<td>3rd peak</td>
<td>545.84</td>
<td>544.77</td>
<td>532.45</td>
<td></td>
</tr>
<tr>
<td>Error</td>
<td>0.12</td>
<td>N/A</td>
<td>0.95</td>
<td></td>
</tr>
<tr>
<td>1st space (cm$^{-1}$)</td>
<td>799.09</td>
<td>585.82</td>
<td>843.27</td>
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</tr>
<tr>
<td>Error</td>
<td>4.21</td>
<td>390.56</td>
<td>46.74</td>
<td></td>
</tr>
<tr>
<td>2nd space</td>
<td>789.70</td>
<td>808.18</td>
<td>667.22</td>
<td></td>
</tr>
<tr>
<td>Error</td>
<td>2.13</td>
<td>61.01</td>
<td>26.55</td>
<td></td>
</tr>
<tr>
<td>1st peak (cm$^{-1}$)</td>
<td>19909</td>
<td>19995</td>
<td>20313</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 3-9: Emission spectra for the montmorillonite clays (SWy-2 and STX-1b) sample series at specified pH values. Spectra are separated by excitation energy and stacked with a slight offset to aid comparison and minimise overlap.
The three distinct species identified by uranyl(VI) sorbed to SWy-1b can be related to previously reported complexes. SWyA resembles species ‘S4’ in work from Chisholm-Brause.\textsuperscript{135} The authors found that this emissive species disappeared upon drying the sample, leading them to correlate this with an outer-sphere complex. SWyB correlates well with ‘S1’ in the same work, and a similar sample in a paper by Wang et al.\textsuperscript{137} the former identifies this species as an inner-sphere complex, possibly bound to a bridging hydroxyl (>Al-OH-Si<) or two adjacent aluminol sites (>AlOH): Wang provided only speculative identification, but suggested a tricarbonate. This presents a conflicting assignment, clearly the species appears to be similar across this work and that of Wang and Chisholm-Brause, but the assignments are entirely different. Firstly, the tricarbonate species is discounted on the fact that these experiments were carried out under carbonate free conditions. Secondly the first peak and vibrational spacing do not match that of a tricarbonate or the kind of bidentate bonding, for example, in QuaA, which would be required for bonding from any carbonate. This leaves the identification from Chisholm-Brause et al.,\textsuperscript{133} of which the Al-O-Si seems most reasonable as the emission properties correlate well to the Al-O-Al seen in boehmite complex BoeB.

SWyC is much harder to define. Variation in the exact position of the peaks changed slightly more than other species when the excitation energy is changed, suggesting that this species is either an average of two weakly emissive and similar sorption complexes or that the single species has many minor differences in arrangement at the surface.
Furthermore, the emission is much weaker than SWyB, so it accounts for an emissive species that is much more easily quenched. This is suggestive of a species that is only weakly bound to the surface.

STxA has large errors in its peak positions and this is primarily a result of minor shifts in peak positions dependent on excitation energy and pH. Despite this, it is detected at every pH and is not observed in any of the other mineral systems studied. Most notably it has a comparatively large vibrational spacing ($1^{st}$ space = 828 cm$^{-1}$, $2^{nd}$ space = 841 cm$^{-1}$), which likely indicates a maintained hydration sphere i.e. an outer-sphere interaction with the interlayer.

STxB compares well to a uranyl(VI) complex sorbed to Al(OH)$_3$ reported by Baumann et al.$^{99}$ STxC is similar to MusD and KaoD, which all correlate very well to SilB. Finally STxD is most like the QuaB complex. STx therefore provides several bonding arrangements for uranyl(VI), which are related to either alumina sites (STxB) or silanol sites (STxC and STxD).

Lifetime data is fairly inconclusive as it only identifies a single exponential decay across all SWy-2 samples, and the presence of several species in chemical exchange at timescales faster than the experiment ($\mu$s) cannot be discounted completely here. Interestingly, the lifetime resolved increases with pH from 4 ($\sim$200 $\mu$s) to 8 ($\sim$530 $\mu$s), and decreases with an increase in excitation wavelength (pH 4 $\sim$200 $\mu$s at $\lambda_{ex}$ = 266 nm, or $\sim$ 155 $\mu$s at $\lambda_{ex}$ = 405 nm).
3.3.5 The luminescence of uranyl(VI) bound to Kaolinite and Muscovite

Kaolinite and muscovite are only somewhat associated to each other (see section 1.4.3). Kaolinite is a 1:1 clay with a large proportion of edge-site interactions. Muscovite, is a 2:1 mineral with extensive basal surface interactions and fairly reduced edge site interactions, relative to the other clay minerals studied. Despite this, the two minerals show some significant similarities in their emission (Fig. 3-11) and excitation (Fig. 3-12) spectra.

Four emissive species are observed for both kaolinite and muscovite samples. The two species labelled KaoD and MusD (Table 3-5) are almost certainly the same species; this species has also been observed in the silica gel samples. Both appear at and above pH 6 and become more dominant at higher pH. Therefore, the species is most likely \( \text{UO}_2\text{OH} \) bound to two separate surface oxides, \([\text{SiO}_2\text{UO}_2\text{OH}]\). Despite similarities in the species emission assignments observed, significant differences exist in the excitation spectra. Muscovite samples have a much larger \( \sim 320 \text{ nm} \) band compared to excitation around the 266 nm band, whereas the opposite is true for kaolinite samples. Lifetime data indicates that muscovite at pH 4 and pH 10 are comparable, represented by a single exponential decay at \( \sim 250 \mu\text{s} \). Muscovite samples at pH 6 and pH 8 are modelled by a double-exponential decay, and display a strong dependence on excitation wavelength.

Table 3-5: Summary of emission parameters determined from low temperature emission measurements (77K) at excitation wavelengths 266 nm, 320 nm and 405 nm for uranyl(VI) sorbed to Kaolinite KGa (Kao) and Muscovite (Mus).

<table>
<thead>
<tr>
<th>comment</th>
<th>4 and 8, all pH 6 only 6,8,10</th>
<th>8,10 4,6 4,10 6,8,10</th>
</tr>
</thead>
<tbody>
<tr>
<td>species</td>
<td>KaoA KaoB KaoC KaoD</td>
<td>MusA MusB MusC MusD</td>
</tr>
<tr>
<td>1st peak (nm)</td>
<td>492.40 497.03 494.28 502.14</td>
<td>492.81 499.56 495.85 481.39</td>
</tr>
<tr>
<td>error</td>
<td>0.06 0.85 0.56 0.43</td>
<td>0.60 0.32 0.00 0.01</td>
</tr>
<tr>
<td>2nd peak</td>
<td>515.08 518.17 516.01 523.41</td>
<td>514.58 518.74 517.23 502.02</td>
</tr>
<tr>
<td>Error</td>
<td>0.79 0.64 0.06 0.40</td>
<td>0.73 0.60 0.56 0.11</td>
</tr>
<tr>
<td>3rd peak</td>
<td>536.43 540.53 540.72 546.61</td>
<td>538.31 N/A 538.66 523.91</td>
</tr>
<tr>
<td>Error</td>
<td>0.22 0.75 0.55 0.99</td>
<td>0.34 N/A N/A 0.24</td>
</tr>
<tr>
<td>1st space (cm(^{-1}))</td>
<td>894.16 826.69 852.17 809.40</td>
<td>858.53 733.80 834.87 832.50</td>
</tr>
<tr>
<td>Error</td>
<td>28.78 36.64 24.95 21.36</td>
<td>4.23 31.23 29.54 10.12</td>
</tr>
<tr>
<td>2nd space</td>
<td>784.95 795.99 885.33 810.49</td>
<td>842.60 N/A 747.07 798.91</td>
</tr>
<tr>
<td>Error</td>
<td>22.43 25.15 16.77 29.44</td>
<td>6.16 N/A N/A 20.49</td>
</tr>
<tr>
<td>1st peak (cm(^{-1}))</td>
<td>20309 20120 20231 19915</td>
<td>20292 20018 20167 20773</td>
</tr>
</tbody>
</table>
Fig. 3-11: Emission spectra for the kaolinite (KAO) and muscovite (MUS) sample series at specified pH values. Spectra are separated by excitation energy and stacked with a slight offset to aid comparison and minimise overlap.
The observation of a silica gel-like surface species is unexpected, as highlighted in section 1.6.4, the dominant modes of interaction of uranyl(VI) with kaolinite and muscovite, as reported in previous studies, are with the AlO⁻ sites (or perhaps, in the case of kaolinite, TiO⁹). The bayerite and boehmite investigations, which present several AlO⁻ sites, do not produce spectra similar to KaoD or MusD. Instead the silica gel species, which only provides bonding to SiO⁻ sites, is nearly identical. This would suggest that binding to silica sites at kaolinite and muscovite surfaces is more significant than previously reported.

Interestingly, the first peak, often around 480 nm, will appear or disappear depending on the excitation energy. For example, in the emission spectrum at λₜₐₖ = 320 nm of muscovite samples the 481 nm peak corresponding to species MusD (and KaoD under the same conditions for kaolinite samples) is not resolvable, but is very clearly present at λₜₐₖ = 405 nm and λₜₐₖ = 266 nm. Curiously, a similar finding was previously reported by Azenha *et al.* for uranyl(VI) sorbed to alumina samples at low temperature, albeit with a first emission peak at a higher wavelength of 485 nm. It remains unclear as to why the emission intensity of this peak would effectively disappear following 320 nm excitation. Supposedly, some minor change in the population distribution at the triplet excited state is resulting in poorer overlap with the wavefunction of the lowest vibrational state of the electronic ground state (S₀₀₀). For example, 320 nm excitation is believed to involve the excitation of a ligand bound directly to uranyl(VI), it is likely that some molecular
rearrangement in the excited state, prior to but sustained for, transfer to the triplet excited state results in this observation.

KaoB appears most like a uranyl(VI) complex sorbed to Al(OH)$_3$ reported by Baumann et al.\textsuperscript{99} the same correlation as drawn to STxB. Both KaoA and MusA are similar and do not correlate at all with any other species identified in this work. The two species have significantly different vibrational spacings, KaoA (894 cm$^{-1}$) has a larger value than MusA (858 cm$^{-1}$), and they appear under different acidities. However, both probably represent a fairly weak interaction with the surface, demonstrated by the large vibrational spacings.
3.4 Conclusions

A comprehensive presentation and discussion of the luminescence excitation, emission and lifetime properties of uranyl(VI) sorbed to the minerals silica (Sil), quartz (Qua), bayerite (Bay), boehmite (Boe) montmorillonite (ST-x and SW-y), kaolinite (Kao) and muscovite (Mus) has been compiled. Several uranyl(VI) species (A-D) have been identified for each mineral system and their spectral properties and most probable identification are summarised in Table 3-6.

Table 3-6: A summary of the emissive species identified and their proposed speciation.

<table>
<thead>
<tr>
<th>Name</th>
<th>Proposed speciation (waters excluded)</th>
<th>Peak positions (nm, rounded)</th>
<th>E$_{00}$ (cm$^{-1}$, rounded)</th>
<th>Present at pH...</th>
</tr>
</thead>
<tbody>
<tr>
<td>SilA</td>
<td>&gt;(SiO)$_2$UO$_2$</td>
<td>495, 523, 546</td>
<td>830</td>
<td>4, 6</td>
</tr>
<tr>
<td>SilB</td>
<td>&gt;(SiO)$_2$UO$_2$OH$^-$</td>
<td>502, 523, 546</td>
<td>810</td>
<td>6, 8, 10</td>
</tr>
<tr>
<td>QuaA</td>
<td>&gt;SiO$_2$UO$_2$OH$^-$</td>
<td>479, 499, 520</td>
<td>820</td>
<td>4, 6, 8, 10</td>
</tr>
<tr>
<td>QuaB</td>
<td>?</td>
<td>507, 529</td>
<td>825</td>
<td>6</td>
</tr>
<tr>
<td>QuaC</td>
<td>?</td>
<td>516, 539</td>
<td>820</td>
<td>8</td>
</tr>
<tr>
<td>BayA</td>
<td>&gt;(AlO)$_2$UO$_2$</td>
<td>479, 493, 514</td>
<td>~830</td>
<td>4, 6, 8, 10</td>
</tr>
<tr>
<td>BayB</td>
<td>&gt;AlO$_2$UO$_2$</td>
<td>483, 501, 521</td>
<td>~780</td>
<td>4, 6, 8, 10</td>
</tr>
<tr>
<td>BoeA</td>
<td>&gt;(AlOH)$_2$UO$_2$</td>
<td>480, 498, 523</td>
<td>755</td>
<td>4, 6</td>
</tr>
<tr>
<td>BoeB</td>
<td>&gt;Al$_2$O$_2$UO$_2$+</td>
<td>485, 505, 526</td>
<td>820</td>
<td>4, 6, 8, 10</td>
</tr>
<tr>
<td>BoeC</td>
<td>&gt;(AlO)$_2$UO$_2$OH</td>
<td>477, 495, 517</td>
<td>765</td>
<td>8, 10</td>
</tr>
<tr>
<td>STxA</td>
<td>(interlayer)UO$_2$OH$^+$</td>
<td>514, 537</td>
<td>840</td>
<td>4, 6, 8, 10</td>
</tr>
<tr>
<td>STxB</td>
<td>&gt;(AlOH)$_2$UO$_2$</td>
<td>499, 519, 542</td>
<td>815</td>
<td>4, 6, 8</td>
</tr>
<tr>
<td>STxC</td>
<td>&gt;(SiO)$_2$UO$_2$OH$^-$</td>
<td>482, 502, 523</td>
<td>830</td>
<td>10</td>
</tr>
<tr>
<td>STxD</td>
<td>silanol interaction</td>
<td>506, 529, 551</td>
<td>840</td>
<td>4, 6</td>
</tr>
<tr>
<td>SWyA</td>
<td>(interlayer)UO$_2^{2+}$</td>
<td>502, 523, 546</td>
<td>800</td>
<td>4</td>
</tr>
<tr>
<td>SWyB</td>
<td>(&gt;AlOSi-)UO$_2$OH</td>
<td>500, 521, 544</td>
<td>~810</td>
<td>6, 8, 10</td>
</tr>
<tr>
<td>SWyC</td>
<td>weak interaction</td>
<td>492, 513, 532</td>
<td>840</td>
<td>6, 8, 10</td>
</tr>
<tr>
<td>KaoA</td>
<td>?</td>
<td>492, 515, 536</td>
<td>895</td>
<td>4, 8</td>
</tr>
<tr>
<td>KaoB</td>
<td>aluminol interaction</td>
<td>497, 518, 541</td>
<td>825</td>
<td>4, 6, 8, 10</td>
</tr>
<tr>
<td>KaoC</td>
<td>?</td>
<td>494, 516, 541</td>
<td>850</td>
<td>6</td>
</tr>
<tr>
<td>KaoD</td>
<td>&gt;(SiO)$_2$UO$_2$OH$^-$</td>
<td>502, 523, 547</td>
<td>810</td>
<td>6, 8, 10</td>
</tr>
<tr>
<td>MusA</td>
<td>?</td>
<td>493, 515, 538</td>
<td>860</td>
<td>8, 10</td>
</tr>
<tr>
<td>MusB</td>
<td>aluminol interaction</td>
<td>500, 519</td>
<td>735</td>
<td>4, 6</td>
</tr>
<tr>
<td>MusC</td>
<td>?</td>
<td>496, 517, 539</td>
<td>835</td>
<td>4, 10</td>
</tr>
<tr>
<td>MusD</td>
<td>&gt;(SiO)$_2$UO$_2$OH$^-$</td>
<td>481, 502, 524</td>
<td>835</td>
<td>6, 8, 10</td>
</tr>
</tbody>
</table>

A clear distinction between a monodentate, >SiO$_2$, and bidentate >(SiO)$_2$ is observed for quartz and silica gel (see Fig. 3-13). The uranyl(VI)-quartz surface complex does not
change as a function of pH, whereas the uranyl(VI)-silica gel complex red shifts as the pH is increased above ~pH 6. This change is associated with the formation of a uranyl(VI) hydroxide surface complex.

Fig. 3-13: The proposed approximate structure for the three major emissive uranyl(VI) species sorbed to SiO₂ minerals. Where a) represents QuaA, b) SilA and c) SilB. Si-O-represents bonding to the bulk SiO₂ structure.

Uranyl(VI) bound to bayerite bears no correlation to uranyl(VI) bound to boehmite. The interaction of uranyl(VI) with bayerite is largely independent of pH. The two identified species are energetically similar inner-sphere complexes which form at edge- or corner-sharing sites. Speculation as to the uranyl(VI) species sorbed to boehmite led to a pH dependent edge site complex and a pH independent interaction with the surface plane.

Fig. 3-14: The proposed approximate structure for the two dominant emissive uranyl(VI) species sorbed to bayerite (α-Al(OH)₃). Where complex a) represents the structure of species BayA and b) represents the structure for species BayB. Al- represents bonding to the bulk Al(OH)₃ structure.

Uranyl(VI) sorption to montmorillonite is diverse; however STx-1b displays character broadly similar to silica gel, owed to its inclusion of interstitial opal-CT. Several identifications are suggested by this data including an outer-sphere interlayer complex for both montmorillonites (STxA, SWyA), a combined Si-O-Al interaction (SWyB), with silanol groups (STxC, STxD) and aluminol sites (STxB).
The identifications made for uranyl(VI) bound to kaolinite or muscovite vary to that reported in the literature, the results reported here suggest that binding to silanol sites are currently under-represented by recent literature assignments.
4 URANYL(VI) SORPTION TO SILICA GEL, SPECIATION FROM PARAFAC DECONVOLUTION OF EXCITATION EMISSION MATRICES

4.1 Introduction

A uranyl(VI) emission spectrum is rarely composed of a single signal from a single uranyl(VI) species. Multiple overlapping signals require deconvolution, as only from the pure signals of single species can the peak shape and maxima be well defined and thus, an indication as to chemical bonding be inferred. It is through the application of advanced signal processing, such as factor analysis, that the underlying signals can be isolated. This chapter will demonstrate the applicability of such techniques for resolving signals from uranyl(VI) bound to silica gel, with the intention of introducing and demonstrating the understanding of such techniques and how they may be applied to more complex systems.

This chapter will summarise the approach taken, and how this can lead to complexation constants with very low associated error. The pure emission signals will be fitted to pseudo-Voight peaks to define the peak maxima and thus vibrational spacing of the uranyl(VI) Raman active total symmetric stretch. This is then compared to the shifts observed for the same samples under a Raman microscope.

4.1.1 PARAFAC

Parallel factor analysis (PARAFAC) is a form of explanatory factor analysis. It is used to accurately estimate the true underlying signals from an overall signal, without prior knowledge of the pure signals. Normally in chemistry, spectroscopic data is generated in two dimensional (second order) arrays. Most of the time several samples are then compared, creating a three dimensional (third-order) array which is difficult to visualise or interpret (i.e. it requires that the data be ‘unfolded’). Interpretation becomes tedious, or misleading, depending by which variable one decides to stack the data. By unfolding, information is lost, and it becomes difficult to differentiate the noise from the signal. Therefore, classical methods are poor at predicting the rank of the variables of 3-way data.

If a 3-way data set follows the trilinear model, as defined by equation (19), it will be possible to explain the data from its total number of underlying components (N) and a non-signal, error component, which represents the noise of the measurement.
\[ S_{ijk} = \sum_{n=1}^{N} A_{in}B_{jn}C_{kn} + Error_{ijk} \]  

In equation (19), the three-dimensional array \( S \) of form \( I \times J \times K \) is composed of the sum of three unique physical parameter sets \( (A, B, C) \) and a residual error component \( \text{Error} \). The method for estimating the components \( A, B, \) and \( C \) is based on alternating least-squares (ALS), which is a non-linear optimization algorithm. ALS estimates \( A \), while assuming \( B \) and \( C \), and then estimates \( B \), while assuming \( A \) and \( C \) and the same for \( C \), repeating this cycle, each time minimizing the error term, until the specified convergence criterion are reached.167

PARAFAC (and the Tucker3 model) was proposed in 1970 as an extension to principal component analysis (PCA).16,168 An extension in that PARAFAC contains an additional diagonal matrix, which is initially guessed and then iteratively solved. The result is a unique solution comprised of a number of components plus any residual noise (see Fig. 4-1).169 This way, the components carry significantly more meaning. The use of PARAFAC in actinide and lanthanide luminescence has increased significantly in the last 5 years,14,170–174 and has largely been accelerated by the development and royalty-free distribution of the N-Way toolbox by Rasmus Bro.169,175

**Fig. 4-1:** A graphical representation of the PARAFAC model. Data is deconstructed into signal components, in this case two, and a final noise component.

There are some issues, mathematically, with using PARAFAC which should be highlighted. When actually fitting a PARAFAC model, the residuals are minimised according to a least squares assessment, adjusting the parameters to give the smallest amount of error. This introduces the ‘local minimum’ error in the energy landscape.

---

1 For example, \( A \) may represent the set of excitation spectra, \( B \) the set of emission spectra, and \( C \) the loadings (concentrations of \( A \) and \( B \) in terms of \( C \))
Ways of minimising the impact of this are explored in this work (see section 4.3.5). Additionally, the number of components must be determined by the investigator, unlike in PCA, where the results are nested. However, the core consistency is widely accepted as a suitable assessment of the number of components, provided any outliers have been accounted for.\textsuperscript{175–177}

\section*{4.1.2 Speciation of uranyl(VI) complexes}

Because PARAFAC produces the loadings of pure species in terms of the experimental variable (the pH in this case), the speciation can be obtained by relating the equilibrium of complexation with the silica gel surface.\textsuperscript{178} Firstly the deprotonation of a silanol, as shown in Equation (20)

\[ > \text{SiOH} \rightleftharpoons > \text{SiO}^- + H^+ \]  

(20)

From the literature (see section 1.6.2) a few possible complexes of uranyl(VI) may form in the pH range 3 - 10 in the presence of silica gel. Equation (21) shows the formation of the first hydrolysis product required for the formation of the related surface complex (23). Equation (22) describes the formation of the neutral surface complex.

\[ \text{UO}_2^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{UO}_2\text{OH}^+ + \text{H}^+ \]  

(21)

\[ \text{UO}_2^{2+} + 2(>\text{SiO})^2- \rightleftharpoons (>\text{SiO})_2\text{UO}_2^- \]  

(22)

\[ \text{UO}_2\text{OH}^+ + 2(>\text{SiO})^2- \rightleftharpoons (>\text{SiO})_2\text{UO}_2\text{OH}^- \]  

(23)

Where \( > \) represents bonding to the bulk of the silica gel. It follows that the formation of the two surface complexes can be described by equations (24) and (25).

\[ K_{f2} = \frac{\text{[(} (>\text{SiO})_2\text{UO}_2^- \text{)]}}{\text{[(} (>\text{SiO})^- \text{)]^2[\text{UO}_2^{2+} \text{]}]} \]  

(24)

\[ K_{f3} = \frac{\text{[(} (>\text{SiO})_2\text{UO}_2\text{OH}^- \text{)]}}{\text{[(} (>\text{SiO})^- \text{)]^2[\text{UO}_2\text{OH}^+ \text{]}]} \]  

(25)

Defining the formation coefficients \( K_{fs} \) will be possible from the PARAFAC output, and a description of the silica gel surface, more specifically, the concentration and pK\(_a\) of the SiO\(^-\) site. As alluded to in section 1.4.2, the silica gel surface is described by two forms of silanol surface sites; external and internal (see Fig. 4.2). Thus, the parameters
summarised in Table 4-1 were used to describe the silica gel surface as a 2-site model, as characterised by Campen et al.\textsuperscript{77}

\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{fig4.png}
\caption{A representation of the two-site model used in the speciation calculations used here. Site 1 (red) indicates external surface sites which are deprotonated even under acidic conditions. Internal surface sites (blue) are fully protonated under acidic conditions. Adapted from reference\textsuperscript{77}.}
\end{figure}

\textbf{Table 4-1: Parameters used in the two site model of the silica gel surface.}

\begin{tabular}{|c|c|c|c|}
\hline
Site 1 & Site 2 \\
\hline
2.5 & pK\textsubscript{a} & 8 & pK\textsubscript{a} \\
\hline
4.75 & sites/nm\textsuperscript{2} & 28.5 & sites/nm\textsuperscript{2} \\
\hline
2.28E+20 & sites & 1.368E+21 & sites \\
\hline
3.79E-4 & Mol sites & 2.272E-3 & Mol sites \\
\hline
0.0379 & Mol/L & 0.2272 & Mol/L \\
\hline
\end{tabular}

\textbf{4.2 Methods}

Please refer to section 2.1 for the methods relating to batch sorption. As before, all batch sorption experiments are conducted in a carbon dioxide-free atmosphere.

As was highlighted in the literature review of uranyl(VI) interactions with silica gel (Section 1.6.2), the time between the first contact of the uranyl(VI) salt solution and the
solid to the end of centrifugation (referred to herein as contact time) is critical to the luminescence properties of this particular system. All samples were therefore timed from the start of sorption (first contact between uranyl(VI) and solid phase) to the end of sorption (centrifugation and supernatant separation). Although every effort was made to achieve a fixed contact time for each sample, the obtainment of accurate pH readings was prioritised along with the requirement for pH equilibration (i.e. a 12 hour no-stray period). The final pH, contact time and % sorption for each sample is listed in Table 4-2 of the results. During preliminary sorption experiments, the amount of salt added due to acidification and basification of the samples was deemed to be negligible even for the highest and lowest pH samples.

Please refer to section 2.3 for details of the Edinburgh Instruments FLSP920 Fluorescence Spectrometer used to collect the excitation emission matrix (EEM) data for this work. Several preliminary investigations were conducted to determine the most suitable parameters for EEM measurements. Following this, excitation and emission monochromators were both set to a width of 1.50 nm. The EEM measurements are composed of 190 emission spectra in the range 250 nm to 440 nm in 1 nm steps, each emission spectra scans from 480 nm to 600 nm in 1 nm steps, which is repeated for the 15 samples covering the pH range 3.00 to 10.00 at 0.50 unit steps. This results in a three-way data set comprising 191 x 121 x 15 values.

4.3 Results

4.3.1 Batch sorption

Sorption was as expected and concordant with that reported in the literature for similar systems. The amount of uranyl(VI) sorbed increases from pH 3.0 (33%) to pH 4.5 (97%) and remains at 100% for samples between pH 4.5 and pH 10.0.
Fig. 4-3: The percentage of uranyl(VI) sorbed to silica gel as a function of pH. Error represents standard deviation (SD) of triplicate measurements. The errors in pH values are not shown but an error of 0.1 pH units is assumed based on the pH probe manufacture guidelines.

The contact time is also reported in hours, as this has been shown to influence the speciation of uranyl(VI) sorbed to silica gel. Curiously, the two site model with its outer site pKₐ of ~2.5 appears to be inconsistent with the sorption data. Since the moles of sorption sites (site 1 = 3.97 x10⁻⁴ M) far exceeds the moles of uranyl(VI) (UO₂²⁺ = 4x10⁻⁶ M), and one would expect 100% sorption much lower than the observed pH of ~4.5.

Table 4-2: A summary of final pH, sorption behaviour and contact time for each sample used to collect EEM.

<table>
<thead>
<tr>
<th>Target pH</th>
<th>3.00</th>
<th>3.50</th>
<th>4.00</th>
<th>4.50</th>
<th>5.00</th>
<th>5.50</th>
<th>6.00</th>
<th>6.50</th>
<th>7.00</th>
<th>7.50</th>
<th>8.00</th>
<th>8.50</th>
<th>9.00</th>
<th>9.50</th>
<th>10.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>Actual pH</td>
<td>2.99</td>
<td>3.49</td>
<td>3.99</td>
<td>4.47</td>
<td>5.07</td>
<td>5.54</td>
<td>6.02</td>
<td>6.54</td>
<td>7.00</td>
<td>7.53</td>
<td>7.95</td>
<td>8.32</td>
<td>9.08</td>
<td>9.46</td>
<td>9.92</td>
</tr>
<tr>
<td>Contact time (h)</td>
<td>49</td>
<td>51</td>
<td>51</td>
<td>47</td>
<td>50</td>
<td>52</td>
<td>48</td>
<td>48</td>
<td>51</td>
<td>99</td>
<td>78</td>
<td>75</td>
<td>49</td>
<td>99</td>
<td>51</td>
</tr>
<tr>
<td>Sorption (%)</td>
<td>33.4</td>
<td>63.7</td>
<td>87.0</td>
<td>97.4</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>
4.3.2 RAW EEM data

Excitation-emission matrices (EEMs) are created by stacking emission spectra for a range of excitation wavelengths with the resulting matrix populated with intensity values. For uranyl(VI) sorbed to silica gel, the main emission is centred around 520 nm, whereas excitation can occur at one of several ‘bands’ from 250 nm to 450 nm. Uranyl(VI) electronic transitions are not sharp like trivalent lanthanides (see Section 1.5), rather they are broad and contain vibrational character. This is true for both the excitation and the emission spectra.

![Excitation Emission Matrix (EEM) of uranyl(VI) sorbed to silica gel at pH 6.02 recorded at 77K.](image)

Fig. 4-4: An Excitation Emission Matrix (EEM) of uranyl(VI) sorbed to silica gel at pH 6.02 recorded at 77K.

Fig. 4-4 shows the excitation emission matrix for the sample of uranyl(VI) sorbed to silica gel at pH 6.02. It is clear that significant vibrational character is present in the excitation and emission modes, with greater intensity (z-axis) at lower excitation wavelengths (higher energies). For this reason, many investigators of uranyl(VI) luminescence use this high energy region (typically the fourth harmonic of a Nd:YAG
laser at 266 nm) in order to increase the intensity of a time-resolved emission measurement.

**Fig. 4-5: Summed excitation spectra of uranyl(VI) with approximately labelled excitation bands.**

By summing the intensity values in the excitation mode, the overall excitation spectrum is observed (Fig. 4-5). The excitation spectrum shows some signs of vibrational character in multiple bands, which are named A-D for convenience. Band A has been previously referred to as the fingerprint region, as it is most commonly associated with the excitation of fundamental electronic absorption (the uranyl(VI) LMCT absorption band) described in section 1.2.1. The higher energy bands, B and C (indicated approximately in Fig. 4-5) are believed to be a result of excitation from a ligand which precedes the fundamental excitation. Band D represents excitation to a continuum state which is related to the UOα bond and therefore only influenced by the overall bond strength of UOα bond and without vibrational character.

By considering the emission spectrum as a function of excitation energy, as in Fig. 4-6 to Fig. 4-8, it can be seen that the emissive species are somewhat similar in peak positions (Fig. 4-6) or selectively emissive (Fig. 4-7), or more complex still (Fig. 4-8).
More generally, it can be seen that the lower pH samples give rise to higher energy emission, over two pH units around pH 6, the emission shifts to a lower energy. This observation is concurrent with the literature previously cited (see section 1.6.2). At low pH, samples have a vibrational resolved excitation at band C, which is not present in high pH samples. Similarly, high pH samples have a vibrational resolved excitation at band B, which is not present in low pH samples. This result has not been previously reported.
Fig. 4-7: Emission spectra for uranyl(VI) bound to silica gel at pH 6.02 ± 0.1 and measured at 77 K. Changing the excitation energy between 320-329 nm in 3 nm steps presents significant variation in the dominant emission signal.

Fig. 4-8: Emission spectra of uranyl(VI) bound to silica gel at pH 6.02 ± 0.1 and measured at 77 K.
4.3.3 Trilinearity

When initially conducting this research, it was assumed that the data was trilinear. In other words, that the data was made up of pure components, each of these pure components would represent a single excitation pattern, single emission pattern and a magnitude (e.g. concentration) that was dependent on the pH. What is clear from the unpacking of the EEM data is that only excitation between 250 nm and 300 nm (band D) would result in a trilinear dataset that could be represented by pure components. In order to proceed, the data matrices were reduced to just band D. This observation has not previously been reported, despite the fact that it is likely true for several other uranyl(VI) systems. One possible explanation requires consideration of the excitation pathways, and how these might result in changes to the emission spectrum.

Consider a single uranyl(VI) sorption complex (SiO)$_2$UO$_2$. The precise positioning of the two SiO$^-$ units relative to the UO$_2^{2+}$ cation is not fixed, after all this system is partially solvated. When the sample is flash frozen in liquid nitrogen, the (SiO)$_2$UO$_2$ complexes do not all align, the freezing is very fast and any deviations that were present before the freeze are expected to be present after the freeze (at least, molecules may have time to relax into a local structural energy minima). The result is a series of uranyl(VI) complexes which conform on average to the same species, (SiO)$_2$UO$_2$, but in fact have slight deviations in the energy gap between the HOMO and LUMO. This is presented pictorially by Fig. 4-9, Fig. 4-10 and Fig. 4-11.

This observation, if corroborated by other uranyl(VI) systems, will require that excitation by narrow band excitation sources (which lasers inherently are) at energies lower than 300 nm be carefully considered to account for this effect. In the case of direct excitation into the uranyl(VI) LMCT absorption (band A), this is an essentially ‘site selective’ excitation and can be used to separate out different uranyl(VI) species if the electronic absorption energies of each species is known.
Fig. 4-9: Four excitation emission scenarios are demonstrated for the luminescence of urany(VI). The system being illuminated contains the single species, \((\text{SiO})_2\text{UO}_2\), but due to the dynamic nature of the system i.e. slight changes in orientation (system is solvated), the energy levels \(S_1\) and \(T_1\) appear at different energies for different specific \((\text{SiO})_2\text{UO}_2\) arrangements. Under narrow excitation in the fingerprint region (labelled \(\lambda_{\text{ex}}=420\) nm), one of these particular oriented species is observed to dominate the emission. However a narrow excitation in the ‘continuum’ region (labelled \(\lambda_{\text{ex}}=275\) nm), results in emission from every orientation, resulting in an averaged emission signal. Excitation and emission to excited vibrational states are excluded in order not to over-complicate the figure.
Fig. 4-10: Emission spectra of uranyl(VI) bound to silica gel at pH 9.92 ± 0.10 at different excitation energies (272, 275 and 278 nm). Each is within the continuum band (region D).

Fig. 4-11: Emission spectra of uranyl(VI) bound to silica gel at pH 9.92 ± 0.10 at different excitation energies. Each excitation wavelength is within the fingerprint band (region A).
4.3.4 PARAFAC

The PARAFAC model was implemented using MATLAB R2017a and a modified version of the ‘N-Way Toolbox’.\(^{169}\)

Within PARAFAC, the number of total components must be specified (as highlighted in section 4.1.1). The literature review for uranyl(VI) and silica gel interactions (section 1.6.2) indicated that the system may consist of 2-components. Indeed the PARAFAC algorithm finds a considerably high core-consistency for the 2-component model, but presents only somewhat reasonable spectra in the emission mode. The first component appears to contain character from at least 2 uranyl(VI) emissions. The 3-component and 4-component models were then attempted; the results of the core consistency from each run are given in Fig. 4-12. The 4-component model produced degenerate emission spectra and a negative core consistency value. However the 3-component model gave a high core consistency of 63% and non-degenerate (i.e. unique) excitation and emission spectra.

![Core consistency vs # of components](image)

*Fig. 4-12: The core consistency values for the PARAFAC model of EEM data stack of uranyl(VI) sorbed to silica gel at pH 3 to 10 in 0.5 pH unit steps. The excitation and emission modes were constrained to non-negativity and the loadings were constrained to unimodality and nonnegativity. Note a value near zero represents an invalid model.*

The 3-component model was then repeated a total of 20 times using randomly generated starting points, half of the runs had unimodality and non-negativity imposed on the excitation mode, the other half had only non-negativity imposed. The two sets of runs
produced core consistency averages of 63% and 64%, respectively. This signifies that the solution is reliable and accurate. The different constraints had little effect on the output. The outputs for the 3-component model are shown in Fig. 4-13 and Fig. 4-14 for the emission and excitation modes respectively. The outputs in the emission mode were fitted using the third derivative as a starting point for the first peak (highest energy peak). These peak positions were then minimised according to a series of five pseudo-Voight curves with the requirement that the gap between successive peaks is less than or equal to the gap before it (the spacing is denoted $\Delta$ in Table 4-3). The excitation mode shows a slight red-shift, which correlates with the red shift in the emission mode for the same species.

**Fig. 4-13:** Emission mode output of the three component PARAFAC model of the EEM data matrix of uranyl(VI) sorbed to silica gel.
Table 4-3: Results of the pseudo-Voight analysis of the emission mode of the three PARAFAC components, see Fig. 4-13. Where Δ represents the difference between the current and previous peak.

<table>
<thead>
<tr>
<th></th>
<th>UO₂</th>
<th>(SiO)₂UO₂</th>
<th>(SiO)₂UO₂OH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Centre (cm⁻¹)</td>
<td>Δ (cm⁻¹)</td>
<td>relative area</td>
</tr>
<tr>
<td>peak 1</td>
<td>20277</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>peak 2</td>
<td>19424</td>
<td>853</td>
<td>100</td>
</tr>
<tr>
<td>peak 3</td>
<td>18586</td>
<td>838</td>
<td>53</td>
</tr>
<tr>
<td>peak 4</td>
<td>17748</td>
<td>838</td>
<td>19</td>
</tr>
<tr>
<td>peak 5</td>
<td>16912</td>
<td>836</td>
<td>2</td>
</tr>
</tbody>
</table>

Fig. 4-14: Excitation mode of the three component PARAFAC model off the EEM data matrix of uranyl(VI) sorbed to silica gel.

The components as a function of sample pH where plotted (circles in Fig. 4-15) and then normalised (lines in Fig. 4-15) to highlight the change in speciation as a function of pH.
Fig. 4-15: The loadings of the three PARAFAC components (20 runs) as a function of pH and the scaled luminescence intensity. Open circles represent the actual loadings output for each sample at each pH, lines represent the normalised intensity.

The three components in Fig. 4-13, Fig. 4-14 and Fig. 4-15 have been labelled as UO$_2$$^{2+}$, (SiO)$_2$UO$_2$ and (SiO)$_2$UO$_2$OH$^-$ using the following reasoning.

The emission properties of the first component (UO$_2$) are similar to the outer-sphere species identified with montmorillonite sample STx-1b identified in section 3.3.3 as STxA. This comparison is particularly noteworthy as the vibrational spacing (~850 cm$^{-1}$ in both) is much closer to that of aqueous uranyl(VI) (~870 cm$^{-1}$); especially considering all other sorption complexes have a vibrational spacing of considerably lower values (<840 cm$^{-1}$). The species STxA was observed at all pH values, including at values below the pH point where the majority of amphoteric adsorption sites are deprotonated and hence cannot favourably interact with uranyl(VI), suggesting an interaction with the interlayer space of the clay. This interlayer interaction maintains at least the first hydration sphere at the equatorial plane of uranyl(VI), which is likely true for the hydrated uranyl(VI) species observed interacting with the silica gel below pH 4.

This emission is notably different to that of the fully aqueous uranyl(VI) cation, suggesting that there is at least some form of interaction with silica gel, probably in the pore space, that is resulting in a change in the HOMO-LUMO energy gap of the uranyl(VI) molecular orbitals.
The second and third species are similar to the species that were identified as sorbed to silica gel in chapter 3. In that case, the species were identified as (SiO)$_2$UO$_2$ at pH 4 and 6 and (SiO)$_2$UO$_2$OH at pH 6, 8 and 10, which matches remarkably well to the loadings plot shown in Fig. 4-15. However, the peak maxima and vibrational spacing values reported in chapter 3 are an average of the emissions resulting from excitation at 266, 320 and 405 nm, which artificially lowers the emission wavelengths observed. This is because the 405 nm excitation results in the non-trilinear emission, described earlier in this section (4.3.3). By averaging emission maxima resulting only for emission spectra with $\lambda_{ex} = 266$ nm, the samples that appear to only contain SiO$_2$UO$_2$OH in chapter 4 and have, perhaps unsurprisingly, the same emission maxima for the same species determined here from the PARAFAC method.

The loadings (Fig. 4-15) were then fit to give the complexation constants using an adapted Newton-Raphson algorithm. The code for implementing this algorithm was adapted for Matlab by Smith and refined by Drobot. It is able to fit the stability constants to a given distribution. The results of the fit are presented in Fig. 4-17 and in Table 4-4.

---

**Fig. 4-16**: A unimodal fit of the loadings of the three PARAFAC components as a function of pH and the total uranium concentration for uranyl(VI) sorbed to silica gel.
Fig. 4-17: A plot of the optimised log(K) values for (SiO)$_2$UO$_2$ and (SiO)$_2$UO$_2$OH for the three component PARAFAC model (20 runs). Error shown is the standard error for the 20 runs.

Table 4-4: The averaged log(K) values as shown in Fig. 4-17.

<table>
<thead>
<tr>
<th>complex</th>
<th>log(K) average value</th>
<th>standard deviation (σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(SiO)$_2$UO$_2$</td>
<td>9.22</td>
<td>0.02</td>
</tr>
<tr>
<td>(SiO)$_2$UO$_2$OH</td>
<td>3.45</td>
<td>0.01</td>
</tr>
</tbody>
</table>

The total symmetric vibrational stretch of the UO$_{ax}$ bond is Raman active. Raman microscopy was used to corroborate the symmetric stretching frequency defined by the uranyl(VI) emission PARAFAC components with those observed by Raman spectroscopy.
Fig. 4-18: A bright field microscopy image of silica gel at pH 6.02, the two locations chosen for Raman measurement are highlighted (above), the Raman response (below) from the two spots highlighted in the upper image and a blank sample at pH 6. D1 and D2 refer to the known ‘defect’ lines from the silica gel structure.\textsuperscript{181,182} The Raman measurement of a sample at pH 6 displays both the Raman active stretching modes of UO\textsubscript{2}\textsuperscript{2+}, labelled $\nu_1$ and $\nu_2$ in Fig. 4-18, the symmetric stretching mode and the deformation mode respectively.\textsuperscript{44} The defect lines D1 and D2 are identifiers of amorphous silica.\textsuperscript{181,182} The symmetric stretching frequency ($\nu_1$) was then fit to two Gaussians in order to compare the values with those identified from the uranyl(VI)
PARAFAC emission spectra, the observed peaks are fit and shown in Fig. 4-19, and tabulated in Table 4-5.

![Fig. 4-19: The two Raman spot spectra between the wavenumbers 795, and 860 cm\(^{-1}\). Two Gaussians are fit to each curve and peak centres are reported in Table 4-5.](image)

<table>
<thead>
<tr>
<th>Raman peak fitting</th>
<th>1(^{st}) peak centre (cm(^{-1}))</th>
<th>2(^{nd}) peak centre (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spot 1</td>
<td>817.8</td>
<td>830.0</td>
</tr>
<tr>
<td>Spot 2</td>
<td>818.0</td>
<td>830.3</td>
</tr>
</tbody>
</table>

The resolved stretching frequencies somewhat match the values produced from the PARAFAC analysis. The (SiO)\(_2\)UO\(_2\) values are 825 cm\(^{-1}\) (luminescence) compared to 830 cm\(^{-1}\) (Raman). The (SiO)\(_2\)UO\(_2\)OH values are 811 cm\(^{-1}\) (luminescence) to 818 cm\(^{-1}\) (Raman). The trend observed is encouraging, and the difference in values may be a result of the low temperature measurement of the luminescence (77 K), whereas all Raman spectra were collected at room temperature. The similar values support the PARAFAC 3-component solution. Raman of lower pH samples (3.5, 4.0) did not resolve the aqueous species, expected to have a stretching frequency of \(\sim 850\) cm\(^{-1}\). Several other features of the Raman spectra are notable. For example, the appearance and
disappearance of the deformation stretch between the two spots in Fig. 4-18. This suggests heterogeneity in between aggregates of silica gel. This theme of microscopic heterogeneity is explored further in chapter 5.

4.3.5 Advanced error estimation using Monte Carlo noise

So far we have assumed that the data is composed of pure underlying signals. To test this, we need to determine if the parameters are truly correlated. This can be improved using a Monte Carlo simulation.¹

To test the accuracy of the model parameters determined by the PARAFAC method, 350 synthetic data sets were simulated and then resolved. This was achieved by taking the parameter output that has the lowest sum of squares and replicating it, and then reintroducing the normal distributed noise of the same variance as the original data. Each new dataset can then be deconvoluted; the standard deviation of these new outputs will be much more representative. The process is demonstrated in Fig. 4-20.

![Diagram showing Monte Carlo advanced noise calculation method](image)

**Fig. 4-20**: A schematic of the Monte Carlo advanced noise calculation method. The initial data set is input into PARAFAC several times. The solution with the lowest (min) $\chi^2$ is selected and labelled $a_0$. The noise of $a_0$ is used to model the generation of new noise which is then added to create a synthetic data set ($D$). Each synthetic data set is then modelled.

¹ To estimate the probability distribution of the PARAFAC output from the ‘true’ signal would require an infinite number of hypothetical data sets, so by increasing the number of outputs it is possible to increase the accuracy of our outputs, providing they are at least close to the ‘true’ value.
using PARAFAC, outputting a new series of parameter sets. $i$ represents the total number of samples, $S$, and $l$ is the total number of synthetic data sets, $D$.

The results of the Monte-Carlo data simulation produce emission, excitation and loadings that confirm the accuracy of the original output. The subsequent optimisation of the $\log(K)$ values are plotted in Fig. 4-21. Remarkably, both the average values and the associated error are identical to the previous assignment (compare Table 4-4 and Table 4-6).

![Fig. 4-21: A plot of the optimised $\log(K)$ values for $(SiO)_2UO_2$ and $(SiO)_2UO_2OH$ for the three component PARAFAC model (350 Monte Carlo simulations). Error shown is the standard error for the 350 Monte Carlo simulated runs.](image)

**Table 4-6: Average and associated error for the $\log(K)$ values presented in Fig. 4-21**

<table>
<thead>
<tr>
<th>complex</th>
<th>$\log(K)$ average value</th>
<th>standard deviation ($\sigma$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(SiO)_2UO_2$</td>
<td>9.22</td>
<td>0.02</td>
</tr>
<tr>
<td>$(SiO)_2UO_2OH$</td>
<td>3.45</td>
<td>0.01</td>
</tr>
</tbody>
</table>

**4.4 Conclusions**

The excitation and emission properties of uranyl(VI) with silica gel in the absence of carbon dioxide can be described by three species. The species were resolved using the EEM of 15 samples in the pH range 3 – 10 and deconvoluting the three dimensional dataset using a three component PARAFAC model. An outer-sphere $UO_2^{2+}$, associated with the pore structure of silica gel, and two inner sphere complexes, $(SiO)_2UO_2$ and $(SiO)_2UO_2OH$ were assigned to the PARAFAC outputs.
From the loadings as a function of pH it was possible to resolve the complexation constants for the two inner-sphere species. Monte Carlo error simulation was used to assess the reported error in the complexation constants, but no improvement was observed, supporting the original assignment. The emission spectra for the three components were analysed using pseudo-Voight peak fitting, the vibrational spacing observed are consistent with the Raman stretching frequencies measured for the same system. This correlation between spectroscopies, luminescence and Raman, improves the confidence in the accuracy of the outputs of the PARAFAC model.

Several excitation bands were discarded prior to PARAFAC analysis. This was due to violation of trilinearity in the relationship between excitation, emission and loading. This observation is justified by considering the selective excitation and emission of complexes that exist in a local energy minima; this selectivity is not observed for excitation into the energy continuum under 250 - 300 nm excitation. Implications for the fitting of emission spectra that use lower energy narrow band excitation (i.e. lasers >300 nm) could be significant enough to cause the incorrect assignment of peak maxima in the emission of uranyl(VI) complexes that are in fact described by several similar energy complexes.
5 URANYL(VI) LIFETIME MICROSCOPY OF UPTAKE TO SILICA GEL, BAYERITE AND MONTMORILLONITE.

5.1 Introduction and objectives

Characterisation of the interaction between uranyl(VI) and mineral surfaces is mainly derived from techniques such as X-ray absorption\textsuperscript{62,95,116} and electronic\textsuperscript{99,137,151} or vibrational\textsuperscript{165,183} spectroscopies which usually measure an average, bulk-state signal. It is the objective of this chapter to explore whether the assumption that these systems can be described accurately from a bulk state signal is suitable, and to what extent can luminescence lifetime be used to study changes in uranyl(VI) speciation across a mineral sample.

![Image showing a 3-dimensional impression of a FLIM/PLIM measurement](image)

**Fig. 5-1:** A 3-dimensional impression of a FLIM/PLIM measurement. A grid structure represents the pixels of the image as a laser scans the surface one pixel at a time. Note that not all pixels are focused onto the mineral, some are focused at mineral edges and others within the mineral bulk. Image generated by the author using SketchUp.

5.1.1 Time-resolved luminescence lifetime imaging microscopy

For more than 3 decades, time resolved luminescence imaging microscopy has been used as a means of observing changes in the chemical environments of fluorescent probes, utilizing the very short lived (nanosecond) lifetimes of the various added chromophores, or naturally fluorescent molecules such as tryptophan in proteins.\textsuperscript{184–186} Fluorescent molecules act as environmental sensors, as their lifetimes are affected by the electronic environment of the molecule. Quenching, temperature, rotational, radiative and non-radiative decay pathways can all affect the lifetime of a fluorophore.\textsuperscript{187} This information can then be used to identify changes in the chemistry at a sub-micron level.
Progression in the field was initially motivated towards minimising the impact of photobleaching, which involves the breakdown of the organic chromophore during its excited state. For example, advancement in the application of time-correlated single-photon counting (TCSPC) resulted in near ideal photon counting efficiencies\textsuperscript{188} permitting very short acquisition times. Transient FLIM permits even faster measurements.\textsuperscript{189} Use of the technique has continued to grow with one reviewer stating 'nearly every great breakthrough in chemistry and physics has aided the development of fluorescence lifetime techniques and a growing number of discoveries in biology and medicine owe their existence to fluorescence lifetime'.\textsuperscript{52}

In support of this, Baggaley \textit{et al}.\textsuperscript{190} note three key advantages of fluorescence over other techniques. (1) Fluorescence is highly sensitive – owed to high photon counting efficiencies, only low concentrations of the emissive species are required. (2) Luminescence microscopy has a high spatial resolution – less than 1µm resolution is possible with a simple optical microscope and resolution is limited only by the diffraction limit of the light involved. (3) Emission is fast – enabling the monitoring of chemical change in real time. The same authors presented the first review of the applicability of using transition metal complexes in place of organic chromophores for FLIM and PLIM. An ideal light-emitting metal complex is one which undergoes ligand-to-metal charge-transfer (LMCT) during excitation. The large metal character of the excited state facilitates spin-orbit coupling (SOC) pathways, which accelerates the rate of intersystem cross (ISC) from the singlet excited state to the triplet excited state and promotes the transition from the excited triplet back to the ground state (phosphorescence i.e. $\Delta S \neq 0$), a transition which is heavily forbidden in organic molecules. For the d-block 2nd and 3rd row metals, phosphorescent complexes with d\textsuperscript{6} electronic character such as [Ru(bpy)\textsubscript{3}]\textsuperscript{2+} \textsuperscript{191} and complexes of Ir(III) and Pt(II) are considered ideal (see ref \textsuperscript{192} for a comprehensive review of d\textsuperscript{6} metals for imaging).
Fig. 5-2: A Jablonski diagram of the fluorescent (blue) and phosphorescent (red) emission processes. Phosphorescence requires inter-system crossing (ISC, dotted line) from an excited singlet ($S_1$) to an excited triplet ($T_1$) state.

All of the advantages of using d-block metals apply equally well to the luminescent f-block elements. Several innovations continue to be published with respect to the use of transition metals and lanthanides, including several combinations of d- and f-block (lanthanide only) luminescent species\textsuperscript{193-195} as well as a demonstration of the capability to monitor up to 9 probes at once (optical multiplexing).\textsuperscript{196}

Crucially, the works cited here are interested in using the d-block (and some lanthanide) metals for better imaging of biological systems, utilizing the long-lived emission of these ions. That is, they use a (often synthesised) luminescent probe in order to infer the chemistry of a biological process. Within this work, the interest lies with the luminescent species itself, uranyl(VI), its lifetime and emission properties are directly indicative of the processes of interest. With this comes the requirement of some technical development, outlined in the next section are summaries of several studies of uranyl(VI) with bayerite ($\alpha$-Al(OH)$_3$), silica gel (SiO$_2$), a mixture of bayerite and silica gel (‘mixture’), and STx-1b montmorillonite.

### 5.2 Terminology and technical development

The FLIM and PLIM data acquired by the TCSPC system can be considered as an array of pixels, each pixel contains 256 time channels and each time channel contains a count of photons for time steps in the luminescence decay. In other words, the FLIM and PLIM measurement delivers images with a decay curve in every pixel, see Fig. 5-3, left.
To obtain a ‘lifetime image’ from these data the fit procedure has to be performed in all pixels of the image, Fig. 5-3, middle figure. The result is a set of amplitudes, \( a \), and lifetimes, \( \tau \), for all pixels of the image, see Fig. 5-3, right.

**Fig. 5-3**: Analysis of FLIM/PLIM data. Left: Raw data, pixels contain decay curves. Middle: Fit procedure, produces the lifetimes and amplitudes for each pixel. Right: Lifetime data, pixels contain the results of the fitting procedure. From TCSPC handbook.\textsuperscript{188}

There are several parameters to consider in order to accurately model the collected data. The bulk of results in this chapter refer to the use of PLIM, so a detailed discussion of the instrument response function (necessary in FLIM) is not required. Accurately modelling the background of PLIM can be difficult, and is considered the most significant impairment to accurate lifetime values.\textsuperscript{197}

**Fig. 5-4**: Left: Bright field image of a sample of bayerite loaded with uranyl(VI) at pH 4. Note the blank area extends to below the image. Right: PLIM intensity image of bayerite loaded with uranyl(VI) at pH 4. The red polynomial highlights the area used to calculate the offset.
An offset is used to remove statistical noise. The noise is assumed to affect each time channel equally, thus a linear offset value in the y-axis can be used to account for it. For a FLIM measurement, the pre-pulse intensity average can be used, but this is not possible for a PLIM measurement. An offset value which overestimates the contribution of noise to the signal will result in the modelling of lifetimes which are shorter than reality, and underestimating the noise will result in longer lifetimes. In this work, the offset value has been calculated for each sample independently, the results of which are summarised in Table 5-1. The precise calculation of the offset value is demonstrated by considering the bayerite pH 4 sample as an example. First, an area of the image is selected which contains no mineral sample (as determined by a combination of bright-field microscope image and detectable PLIM, see Fig. 5-4). In this example, 1986 blank area pixels were averaged over the range $T_1=27$ to $T_2=250$, where $T_n$ refers to the time channel $n$, to give an offset value of 35.06. By using Eq. (26), the pseudo offset value is determined to be 1156.94 photons per time channel. The offset used in the PLIM is then determined by Eq. (27), and depends on the binning factor used, in this case it is 2.98 photons per time channel.

$$[Pseudo\ offset] = \frac{[background\ average]}{[blank\ area\ (pixels)]} [total\ pixels]$$  \hspace{1cm} (26)

$$[offset] = \frac{[background\ average]}{[blank\ area\ (pixels)]} (2[binning\ used] + 1)^2$$  \hspace{1cm} (27)

Note in Eq. (27) the term 'binning used'. In the analysis of FLIM and PLIM data, binning refers to the inclusion of neighbouring pixels in order to raise the total number of photons in the decay trace to a number great enough to accurately model the data (see Fig. 5-5).
Next, the number of exponentials required to model the signal needs to be determined. The $\chi^2$, which is the sum of the residual, is minimised during fitting, i.e. it is used to solve the exponential decay model. A value close to 1 is considered accurate, however this value can sometimes be misleading hence the shape of the residual, which should fluctuate randomly about zero, is also considered. To remove any pixels from the PLIM which are not a result of uranyl(VI) emission, a threshold value is determined based off of the background calculation. Finally, it is important to note that the data were collected over several user access trips at the Central Laser Facility at Rutherford Appleton Laboratory, between which a fluctuation in noise was observed. For example, the silica gel samples were measured at (Feb 2016) a different time to the bayerite samples (Nov 2015), the background is slightly different and this is reflected in the offset calculation tabulated in Table 5-1.

**Table 5-1: A table of input parameters for fitting PLIM of loaded samples. *value rounded from a representative pixel**

<table>
<thead>
<tr>
<th>mineral</th>
<th>pH</th>
<th>Binning used</th>
<th>components</th>
<th>PLIM offset</th>
<th>Photons in trace*</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bayerite</strong></td>
<td>4</td>
<td>6</td>
<td>2</td>
<td>2.91</td>
<td>3000</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>6</td>
<td>2</td>
<td>2.88</td>
<td>3000</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>2</td>
<td>1</td>
<td>1.85</td>
<td>4000</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>6</td>
<td>2</td>
<td>3.30</td>
<td>3000</td>
</tr>
<tr>
<td><strong>Silica gel</strong></td>
<td>4</td>
<td>4</td>
<td>2</td>
<td>2.36</td>
<td>2000</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>2</td>
<td>2</td>
<td>0.99</td>
<td>2000</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>1</td>
<td>2</td>
<td>1.03</td>
<td>10000</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0</td>
<td>1</td>
<td>2.65</td>
<td>2500</td>
</tr>
</tbody>
</table>

*Fig. 5-5: A graphical representation of binning. The examined pixel (pink) may include neighbouring pixels (yellow), whose decay trace is added to the examined pixel to increase the signal and improve the model accuracy.*
Results and Discussions

The interaction of uranyl(VI) with each mineral phase is considered in turn and comparisons and conclusions are drawn between them. Discussions about silica gel, which are demonstrated first, are slightly more elaborative to aid reader comprehension of the data.

Readers interested in the use of intensity images, as well as the response observed from blanks, or a more elaborated discussion of the fitting procedures and input parameters are encouraged to consult the Appendix (8.3). The most relevant information however, is briefly summarised here. Blank samples, that is samples prepared identically but in the absence of uranyl(VI) do not present resolvable PLIM, this is to be expected as none of the mineral phases considered have naturally phosphorescent mineral phases within them, more notably it represents that only a low level of background light enters the PLIM photon counting instrumentation over the time period of a normal PLIM measurement (10 minutes). FLIM however shows considerable scatter, this is typically represented by a spike in the time resolved decay and generally not representative of a decay. A more detailed discussion of FLIM of these minerals, including a comparison between blanks and loaded samples reveals that FLIM may be useful in identifying the mineral composition with respect to the lifetime of uranyl(VI) (i.e. contrasting that of the FLIM and PLIM), although this is complicated by the phosphorescence of very bright samples. However, this is encouraging and demonstrates that the combined, simultaneous measurement of FLIM and PLIM may aid the more complex identification of interactions of heterogeneous mineral phases and mixtures.
5.3.1 Uranyl(VI) uptake onto mineral systems.

The sorption behaviour of uranyl(VI) with the minerals bayerite, silica gel, a 50:50 mixture of bayerite and silica gel (herein referred to as mixture) and montmorillonite are consistent with section 3.3.1 and the literature therein and is tabulated in Table 5-2.

Table 5-2: The equilibrated pH and % sorption for each sample studied; estimated error in pH readings is ±0.10 pH units. *pH 2 is below the sorption edge of these systems, hence the very low sorption values, therefore the pH 2 samples were not measured by FLIM/PLIM.

<table>
<thead>
<tr>
<th>Target pH</th>
<th>Bayerite</th>
<th>Silica gel</th>
<th>Montmorillonite</th>
<th>mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Final pH</td>
<td>% on mineral</td>
<td>Final pH</td>
<td>% on mineral</td>
</tr>
<tr>
<td>2*</td>
<td>2.11</td>
<td>2.87%</td>
<td>2.02</td>
<td>0.00%</td>
</tr>
<tr>
<td>4</td>
<td>4.32</td>
<td>42.42%</td>
<td>4.02</td>
<td>66.95%</td>
</tr>
<tr>
<td>6</td>
<td>6.38</td>
<td>100.00%</td>
<td>5.68</td>
<td>100.00%</td>
</tr>
<tr>
<td>8</td>
<td>8.01</td>
<td>100.00%</td>
<td>8.19</td>
<td>100.00%</td>
</tr>
<tr>
<td>10</td>
<td>9.82</td>
<td>99.30%</td>
<td>9.76</td>
<td>100.00%</td>
</tr>
</tbody>
</table>

5.3.2 Time-resolved emission spectra from PLIM

By diverting the emission light to a spectrometer, the steady-state emission spectrum from a specific pixel can be recorded, referred to herein as spot spectra. Spot spectra are recorded after a specified time-delay, hence time-resolved. It was found that no significant variation in emission position was found by changing this delay. Additionally, this work found no significant variation in the observed emission at different positions within the frame of any of the samples studied. The recorded spectrum from representative areas are shown in Fig. 5-6.
5.3.3 Uranyl(VI) sorbed to silica gel studied using PLIM

All silica gel samples were measured over a PLIM time window of 10 µs to 190 µs, a blank sample was measured by both FLIM and PLIM in order to account for the intrinsic background emission from silica gel (see Section 5.2 for more detail).

The lifetimes from each PLIM map for the silica gel sample set are shown in Table 5-3. These averages may be a useful comparison to bulk state luminescence. In some cases the values reported here correlate well with those reported elsewhere. For example, Lopez et al.\textsuperscript{112} found two lifetimes at pH 9, a minor component at approximately 55 µs

*Fig. 5-6: Uranyl(VI) emission spectra collected at the most intensely phosphorescent spots in PLIM maps. Dotted lines included to guide the eye, values arbitrarily chosen.*
and a major component at \( \sim 250 \mu s \), with the minor component disappearing after 1.5 hours. This is comparable to the lifetime mean (54.62 \( \mu s \)) at pH 6, reported in this work. Perhaps what Lopez observes is this component, which is stable at pH 6, but unstable at higher pH, and hence it disappears from the measurement after a few hours. The longer, major component compares well with component 2 at pH 8 and the only component detected at pH 10.

<table>
<thead>
<tr>
<th>sample</th>
<th>component (( \tau ))</th>
<th>( \tau - \sigma )</th>
<th>( \tau ) mean (( \mu s ))</th>
<th>( \tau + \sigma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 4</td>
<td>1 of 2</td>
<td>-1.34</td>
<td>7.92</td>
<td>+1.31</td>
</tr>
<tr>
<td></td>
<td>2 of 2</td>
<td>-9.46</td>
<td>47.41</td>
<td>+9.16</td>
</tr>
<tr>
<td>pH 6</td>
<td>1 of 2</td>
<td>-1.91</td>
<td>8.01</td>
<td>+0.99</td>
</tr>
<tr>
<td></td>
<td>2 of 2</td>
<td>-9.21</td>
<td>54.62</td>
<td>+9.19</td>
</tr>
<tr>
<td>pH 8</td>
<td>1 of 2</td>
<td>-10.29</td>
<td>29.64</td>
<td>+5.25</td>
</tr>
<tr>
<td></td>
<td>2 of 2</td>
<td>-107.44</td>
<td>241.05</td>
<td>+74.39</td>
</tr>
<tr>
<td>pH 10</td>
<td>1 of 1</td>
<td>-33.53</td>
<td>245.05</td>
<td>+32.44</td>
</tr>
</tbody>
</table>

\( \text{Table 5-3: The average lifetime values for each PLIM measurement of uranyl(VI) sorbed to silica gel at pH 4, 6, 8 and 10. } \sigma \text{ represents the standard deviation in either the positive or negative direction from the average. Comparing } \pm \sigma \text{ can provide an impression of a normal Gaussian distribution or a skewed distribution. In the event of a skewed distribution, } \pm \sigma \text{ will be significantly different, this is important in identifying whether the variation across the surface is reasonably represented by the mean (i.e. } |\pm \sigma| = |\pm \sigma| \text{) or not (i.e. } |\pm \sigma| \neq |\pm \sigma|\).}

Kowal-Fouchard et al.\(^{120}\) found three lifetime components for a similar sorption system, and although the lifetimes reported are significantly different, a similar trend is observed. The lifetimes reported were 65 \pm 6 \( \mu s \), 180 \pm 20 \( \mu s \) and 400 \pm 30 \( \mu s \). The latter only appears at higher pH. These species are assigned as \( \text{UO}_2\text{H}_3\text{SiO}_4^+ \) on \( \text{SiO}_2 \), \( \text{UO}_2^{2+} \) on \( \text{SiO}_2 \) and \( (\text{UO}_2)_n(\text{OH})_m(2n-m)^+ \) on \( \text{SiO}_2 \). Although this speciation is unlikely, following recent computational and modelling work\(^{131}\) (more detail and discussion is provided in section 1.6.2), the identification of three unique lifetimes correlates to the means in Table 5-3. Also included in Table 5-3 are the standard errors in the calculation of the mean, and to what extent the mean accounts for the distribution to a higher or lower value. In other words, if the distribution is skewed (i.e. non-Gaussian) to a lower mean, the \( \tau - \sigma \) will be less negative than the \( \tau + \sigma \) value is positive. The implications of skew (or lack thereof) require consideration of the PLIM images themselves and these are discussed in turn.
Silica gel at pH 4 was weakly phosphorescent and required a binning factor of 4 to give ~2000 photons per trace. The lifetime map is modelled to a double exponential, the images from $\tau_1$ and $\tau_2$ and their lifetime distributions are displayed in Fig. 5-7. Attempting a triple exponential fit gave no improvement in the $\chi^2$ or the shape of the residual. The distributions appear normal distributed about a value of 8.0 µs and 47 µs for $\tau_1$ and $\tau_2$, respectively. Both distributions are very broad, however close inspection reveals that the luminescence lifetime of certain pixels form into groups, which amount to micron sized deviations in lifetime within the silica gel aggregates.

![Image](image-url)

*Fig. 5-7: PLIM for uranyl(VI) sorbed to silica gel at pH 4.02. Colouring is continuous, the distribution graphs (histograms, right) represent 95% of the calculated lifetimes, and values outside this range are assigned red (low) or blue (high).*

The local concentration of uranyl(VI) can influence the luminescence intensity, this in turn can influence the perceived lifetime. Thus one must account for the variation in
intensity recorded in the PLIM channel, which will indicate the variation in local concentration of uranyl(VI). Only once this is accounted for can change in the observed lifetime be attributed to changes in the local environment of uranyl(VI). For the pH 4 sample, the intensity of emission varies by 5% within a silica gel aggregate, with different aggregates varying by up to 25%, most notably, the intensity at the edges of aggregates is markedly less intense, by up to ~50% (Fig. 5-8). This compares to a <30% change in lifetime within the aggregates, ~25% between different aggregates and up to ~60% from the centre to the edge of an aggregate. Thus the drop in lifetime between aggregates and towards the edges of an aggregate is a product of the lower concentration of uranyl(VI) and does not necessarily indicate a change in speciation. However the variation in lifetime within aggregates is significant, and indicates micron-sized differences in the environment of the uranyl(VI) cation.

![Image](image_url)

**Fig. 5-8:** A side-by-side comparison of the intensity image (left) with the lifetime fit ($\tau_2$) (right) of the same uranyl(VI) bound to silica gel at pH 4 PLIM image. The image on the right does not contain intensity information, hence the colour contrast is at 100%. The intensity image shows the variation between silica aggregates and within aggregates – see text for more details.

The micron-sized deviations in lifetime appear to have a more significant influence on the longer lived species ($\tau_2$) than the shorter lived ($\tau_1$). The results of chapter 4 indicate two species present in equal concentration at pH 4, one being a solvated outer-sphere complex, mostly associated with the hydrated pore space of the silica gel, and the second the inner-sphere complex ($\text{SiO}_2\text{UO}_2^-$. This identification fits this PLIM data; $\tau_1$ likely
represents the shorter, more easily quenched luminescence of the outer-sphere species and $\tau_2$ represents the longer lived, more sterically protected luminescence of the inner-sphere complex. It is likely that the inner-sphere complex is more varied because it is more affected by slight changes in the local structure of the silanol surface groups, whereas the hydrated species, only associated with the surface through weaker interactions, is less affected.

**Silica gel at pH 6** required a binning factor of 2, affording $\sim$2000 photons per trace. The PLIM was modelled to a double exponential decay and lifetime distributions appear normal about an average value and at approximately the same $\tau$ as the pH 4 samples. However, the PLIM at pH 6 displays much higher intensity and affords lower binning, despite providing similar lifetime values and the similar micron-sized deviations across the silica gel.
Fig. 5-9: The PLIM of uranyl(VI) bound to silica gel at pH 5.68. Modelled using a double-exponential. The microscopy image (left) and associated lifetime distribution (right) are shown for both the first and second exponential terms ($\tau$), for more detail consult Fig. 5-7 caption.

The similarity between pH 4 and pH 6 in these samples suggest very similar speciation, both samples indicate two species spread relatively evenly across silica gel. Therefore, a discrepancy exists between the low temperature excitation-emission based identification of chapter 4 and the room temperature lifetime identification of this chapter. The former notes a significant change between pH 4, from an outer-sphere and inner-sphere speciation to two inner-sphere species. In addition to the obvious change in measurement temperature, the samples are not identical, in fact the final pH of this pH
6 sample was in fact pH 5.68, which is low. Despite this, no aqueous species is detected above pH 5, in chapter 4. This discrepancy questions the certainty in the identification of an ‘outer-sphere’ species. Such a short lifetime (8.01 µs) is very unlikely to be an inner-sphere species bound to silica. Thus the lifetime suggests it is almost certainly outer-sphere. Several factors, including the vibrational properties and comparisons to aqueous chemistry are discussed at length in the thesis conclusions (chapter 6).

The second longer lived species correlates well with the pH 4 PLIM identification of the longer-lived species, and with the presence of (SiO)₂UO₂OH in both, as identified by low temperature EEM spectra (chapter 3). However, at this pH, the species (SiO)₂UO₂OH was expected but not observed, indicating a discrepancy between the data sets.

Silica gel at pH 8 afforded even greater detail due to an increase in intensity of emission. A low binning value of 1 was used, thus each pixel represents an area of ~1.08 µm² in the x-y plane and each trace has ~6000 photons, more than adequate for a double exponential fit. The PLIM display a splitting of the lifetimes in the τ₁ and τ₂ modes, suggesting a total of four significant lifetimes. The distribution of a₁ is also bimodal, with the shorter lifetime in both instances (that is, the shorter of τ₁ and the shorter of τ₂) contributing broadly ~30% and the longer contributing sharply ~ 70%. Furthermore, different areas of the image appear to be effected to different extents, as if the silica gel aggregates have been selectively altered by the increase in pH.

Enabled by the low binning factor of this sample, the deviation in the lifetimes at the submicron level becomes much clearer; the distributions of the previous samples were normal (aka, unimodal), however they may have been incorrectly identified, and may be bimodal in light of this more intensely emissive sample. This clear bimodal distinction in lifetime of a double exponential has never been observed in a uranyl(VI) sample and highlights a powerful advantage of the PLIM technique.

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¹ a₁ represents the amplitude of the first lifetime (τ₁), it can be used to indicate the intensity contribution to the overall observed intensity. It somewhat correlates to concentration.
Fig. 5-10: The PLIM of uranyl(VI) bound to silica gel at pH 8.19. Modelled using a double-exponential. The microscopy image (left) and associated lifetime distribution (right) are shown for both the first and second exponential terms ($\tau$), for more detail consult Fig. 5-7 caption.

The value of $\tau_1$ is no longer in the range of lifetimes commonly reported for aqueous uranyl(VI), representing a significant change such as the formation of an inner-sphere species. It is possible that the shorter lived component identified at pH 4 and 6 previously associated, for example, with protected SiOH sites, become an inner-sphere complex, perhaps as a result of the deprotonation of well protected inner sorption sites.\(^1\)

\(^1\) This refers to the distinction in silanol sites as outlined in the introduction (1.4.2) and by reference 77. It was found that a more protected form of ‘inner’ silanol sites only become deprotonated above pH 6.5.
Silica gel at pH 10 is more intensely emissive than the pH 8 sample. A binning factor of 0 affords ~2000 photons per trace and the PLIM is modelled by a single exponential.¹

Fig. 5-11: The PLIM of uranyl(VI) bound to silica gel at pH 9.76. Modelled using a single-exponential decay. The microscopy image (left) and associated lifetime distribution (right) are shown, for more detail consult Fig. 5-7 caption.

The lifetime distribution in Fig. 5-11 is clearly broad and covers a wide range of values. It’s possible that the collection window was too short to correctly model this data, but longer ranges would require considerable modifications to the experimental set up and effect continuity of the data set. Regardless, the image contains a shorter lived species which dominates at the edges of aggregates and the appearance of a single dominant species in the bulk phase of the silica gel is congruent with the finding of chapter 4 for samples at pH 10.

All of the silica gel samples display a considerable amount of heterogeneity in the lifetime at a microscopic level, which has not previously been detected by studies of this sorption system. This heterogeneity is observed as micron sized deviations about the average lifetime value. These deviations are likely a result of slight changes in the orientations of

¹ This figure is effectively at the diffraction limit for this form of measurement (see section 1.1 in reference 204). It is at the limit of PLIM to resolve microscopic deviations in a uranyl(VI) sample.
uranyl(VI) with respect to the silica gel surface, affecting the availability of quenching modes.

For samples below pH 10, two dominant species are present, although the values of both $\tau_1$ and $\tau_2$ rise slightly with pH, the distinction between them remains relatively constant, until pH 10, when the presence of a shorter lived species is absent. A similar distinction at high pH has been reported previously, and is believed to be an interaction of uranyl(VI) hydroxide with two distinct deprotonated silanol sites $[\text{SiO}_2\text{UO}_2\text{OH}]^-$.

An important distinction between these results and the results of chapter 3 is that of contact time. All of the PLIM measurements were made a week after the sorption was concluded, due to the requirement for transporting samples between Manchester and Rutherford Appleton Laboratory. It is possible that the added time between sorption and measurement affects the equilibrium of the speciation.
Fig. 5-12: The lifetime distributions of all the PLIM samples for uranyl(VI) bound to silica gel. The y-axis represents the number of pixel. The lifetime values in µs are represented on a \( \log_{10} \) scale to aid comparison.

Fig. 5-12 presents the extent of overlap between the lifetime distributions of each PLIM result and therefore the degree of similarity of the lifetimes of the uranyl(VI) silica species and by extension the possible similarity in chemical speciation. The overlap between pH 4 and 6 is clear (black and red traces), especially for the shorter lived component, and only slightly longer as the pH increases at pH 6, this indicates that the quenching of the shorter lived species is likely not controlled by proton concentration, whilst the longer lived species is at least partially controlled by proton concentration. This suggests that the longer lived species has a stronger interaction with the amphoteric surface silanol groups, at least compared to the shorter lived species. The pH 8 sample represents considerable heterogeneity within sample aggregates and the bimodal distribution of both \( \tau_1 \) and \( \tau_2 \), implying a total of four distinct lifetimes and therefore species. The pH
8 sample appears to be a significant point of change for the uranyl(VI) silica gel system, even displaying heterogeneity between aggregates, suggesting the transition occurs inconsistently. This contrasts significantly to the single long lived lifetime observed at pH 10, which displays a significantly more quenched species at the aggregate edge, although this is likely the same species across the sample; the quenching experienced by this species is more pronounced likely because of poorer steric protection from the fast kinetics of solvent water exchange and/or excited state reactions.

5.3.4 Uranyl(VI) sorbed to bayerite studied using PLIM

The properties of bayerite and literature on its interaction with uranium are discussed at length in sections 1.4.1 and 1.6.1, respectively, but short summaries are included here.

Bayerite, α-Al(OH)₃ forms an octahedral sheet like structure, each aluminium octahedral plane ‘sandwiched’ between a double layer of hydroxyl groups, sheets are then tightly held together through hydrogen bonding. This results in two major forms of hydroxyl available for the binding of uranyl(VI) (and other metal ions), the doubly coordinated hydroxyl (Al)_2O-H (with a pK_a for deprotonation between 2 and 4)⁶⁴ and the single coordinated hydroxyl AlO-H (pK_a of deprotonation between 7 and 9).⁸⁰ The former is most commonly associated with the basal plane and the later with edge sites. The predominant mode of interaction is anticipated to be with the edge sites.

It was reported that EXAFS studies show uranium equatorial oxygens (UO_eq) are split, suggesting uranyl(VI) is sorbed via inner-sphere bonding, the same report found both mononuclear and polynuclear species.⁹⁵ Two additional EXAFS studies found no splitting in UO_eq bonding.¹⁰³,¹⁰⁵ However, both observe large Debye-Waller factors, suggesting uncertainty in the reported bond distances and coordination numbers in this area. Luminescence measurements were reported within the pH range 5.0 – 8.5 and show a biexponential decay of approximately 0.33 µs and 5.6 or 7.26 µs.⁹⁹ A separate luminescence study found lifetimes of 9 µs and 31 µs as well as longer 85 µs and 210 µs lifetimes.¹⁰³ Both studies reported no spectral shift in the position of the uranyl(VI) emission bands. A separate study used a form of factor analysis and multi curve resolution to identify 4 species from cryogenic time-resolved emission spectra. The authors reported that AlO-(UO₂)⁺ dominated the emission below pH 5 and AlO-(UO₂)OH⁰ above pH 5, with another species only present at low ionic strength.
(electrostatically bound UO$_2$(OH)$_3^-$) and a final poorly resolved species. DFT studies showed that sorption to the basal plane of bayerite is uncompetitive, but sorption to edge and corner sharing sites is almost equally energetically competitive, suggesting the presence of both.

The PLIM time windows used were approximately 1 to 12 µs for pH 4 and 2 to 33 µs for the remaining three samples, lifetimes of uranyl(VI) above this range may be present but at concentrations too low to be studied by this method.

PLIM of uranyl(VI) bound to bayerite at pH 4 is weakly phosphorescent, like the other pH 4 samples. A binning factor of 6 was employed, resulting in ~3000 photons per pixel trace. The PLIM is well modelled by a double exponential decay, with bimodal variation in both the shorter ($\tau_1$) and longer ($\tau_2$) lifetime values, resulting in four dominant lifetime values. The colouring used in Fig. 5-3 is chosen to highlight the bimodal nature of the lifetimes in both the $\tau_1$ and $\tau_2$ components and to highlight the continuity in the positioning of the $\tau_1$ and $\tau_2$ lifetime values.
As mentioned in 5.3.3, the identification of 4 significant lifetimes and the identification of two significant binding sites is a major advantage of the PLIM technique for this kind of system. In this case the changes are significant enough to cause clear changes to the lifetimes. It should be noted that the lifetimes in the $\tau_1$ window are short enough to correlate well with the aqueous chemistry of uranyl(VI) at this pH, suggesting an outer-sphere sorption complex. Considering the energetics of interaction at pH 4, $\tau_2$ may correlate to an inner-sphere complex such as AlO-(UO$_2$)$_2^+$, the bimodal distribution in
lifetime may relate to the predominance of edge sharing species of either the mononuclear or binuclear complex.

**Bayerite at pH 6** is approximately as emissive as the pH 4 sample, affording a binning value of 6 and ~3000 photons per trace (Fig. 5-14).

---

**Fig. 5-14:** PLIM and lifetime distribution of uranyl(VI) bound to bayerite at pH 6.38. The microscopy image (left) and associated lifetime distribution (right) are shown for both the first and second exponential terms (τ), for more detail consult Fig. 5-7 caption.
The same bimodal relationship in $\tau_2$ is observed as with the pH 4 sample. The only difference appears in $\tau_1$, which is represented by an additional component around 8 $\mu$s, bringing the number of discernible binding sites to three for the $t_1$ component.

Following from the previous argument, the additional lifetime could be due to the change in solution chemistry observed at pH 6, which becomes more complex. The positioning of the species, towards the edges of the brighter aggregates, suggests these species are more influenced by the aquatic chemistry than those species more clearly associated to the bayerite. This is the opposite effect that was observed for the uranyl(VI) bound to silica gel at pH 10 sample. Compared to silica gel, sorption of uranyl(VI) to bayerite is much more likely to form polynuclear species (as the number of sites per nm area is much lower), which likely have a longer lifetime than their mononuclear counterparts, suggesting a greater presence of polynuclear species towards the edges of some of these aggregates. However, shorter lifetime species are also present towards the edges of other aggregates.

The PLIM of uranyl(VI) bound to bayerite at pH 8 is much more intense than the pH 4 and 6 samples, affording a binning of 2 with $\sim$4000 photons per trace, where each trace is modelled best by a single exponential decay (Fig. 5-15).
This single decay can be divided into at least two significant binding modes, one of which is considerably more intense and results in an emission with a lifetime of between 30 and 40 µs. The majority of emissive pixels are occupied by a sharp distribution at ~10 µs, which correlates with the dominant component in $\tau_2$ of the pH 6 and pH 4 samples. The much brighter and longer lived component is the result of a uranium crystalline phase, which has precipitated on the surface of the bayerite, this can be identified by the stark increase in emission signal intensity (Fig. 5-15), and the large blue shift in the measured emission spectrum, where the emission maximum is shifted from 504 nm compared to 525 nm (Fig. 5-17). Furthermore, the spot spectra of this longer lived component is vibrationally much more well resolved and is similar to a uranyl(VI) ionic salt phase. The energy between the $E_{0.0}$ and $E_{0.1}$ transitions are measured as 780 cm\(^{-1}\) (compared to that of 700 cm\(^{-1}\) for the short lived emissive species).

The PLIM of uranyl(VI) bound to bayerite at pH 10 is about as intense as the pH 4 and pH 6 samples (i.e. a binning of 6 and photon trace of ~3000), it is best fit by a double exponential decay.
There is some evidence to suggest multiple binding sites, such as the clustering of blues and reds (Fig. 5-16). However in this case the distinction is not as clearly observed in the lifetime distribution, which forms a single normal like distribution about a value of 1.75 and 15 μs for $\tau_1$ and $\tau_2$, respectively. It appears as though the shortest lived component that featured prominently in the pH 4 and pH 6 samples (at below 1.5 μs) is significantly reduced, suggesting this lifetime is responsible for an interaction which is not present at higher pH, e.g. an interaction with the protonated form of the alumina surface. Likewise, if we compare the pH 8 $\tau$ distribution with the $\tau_2$ of pH 10, the distribution somewhat matches the bulk of the sample (between 10 and 20 μs), but without the prominent spike at 10 μs, again suggesting the absence of some form of interaction at pH 10, compared to pH 8.
Fig. 5-16: PLIM and lifetime distribution of uranyl(VI) bound to bayerite at pH 9.82. The microscopy image (left) and associated lifetime distribution (right) are shown for both the first and second exponential terms (τ), for more detail consult Fig. 5-7 caption.

The bayerite samples are considerably more complex than the silica gel samples, several much shorter and well characterised lifetimes are identified from these data, and some indication as to their dependence on pH is evidenced.
Fig. 5-17: Spot spectra from PLIM samples of uranyl(VI) sorbed to bayerite. Spectra obtained from various points in the PLIM image without significant change in the peak positioning within the emission window. Note the reduction of noise in the pH 8 sample, a result of precipitation of a uranyl(VI) crystalline phase on the surface of the bayerite, which produces a much more intense and blue shifted spectrum with respect to the pH 6 and pH 10 samples. Also note the high energy contribution at 475 nm for pH 6, which is absent at pH 10, which corroborates observations from reference 96.

In accord with the literature reported for comparable systems, the sample at pH 4 is postulated to be both an outer sphere sorbed complex (in $\tau_1$) and the $\text{>AlO-}$UO$_2^+$ complex (in $\tau_2$). The variation within lifetimes suggests the bayerite surface offers two dominant binding modes for the two uranyl(VI) species at pH 4. The two modes do not vary in uranyl(VI) emission intensity or emission peak positioning (at room temperature), but importantly, vary considerably in lifetime, suggesting that the availability of quenching modes is significantly different for the two sites, the effect to quenching is of equal magnitude to both the outer and inner-sphere sorbed complexes. This would suggest that the observed difference is due to the aggregation of the bayerite, affording variation in the interlayer space and thus extent of hydration. This same effect is observed for the pH 6 sample, with the addition of a hydrolysed uranyl(VI) species which
forms an outer-sphere complex (represented by $\tau_1$ in Fig. 5-14). Quite remarkably, these significant differences in luminescence lifetimes are not anticipated by examination of the spot spectra, (and indeed the bulk spectra), which further highlights the uniqueness of lifetime image mapping to reveal otherwise masked speciation information. A uranyl(VI) containing precipitate is observed to form at pH 8, which dominates the emission and lifetime properties. The sorption at pH 10 is significantly different to other samples, owed to the full deprotonation of all aluminol sites. At this pH, a similar degree of lifetime variation is observed, which may also be due to the formation of variably sized inter-particle spaces.

![Fig. 5-18: The lifetime distributions of all the PLIM samples for uranyl(VI) bound to bayerite. Lifetimes (µs) are represented in a log$_{10}$ scale to aid comparison.](image)

### 5.3.5 Uranyl(VI) sorbed to a mixture of silica gel and bayerite studied using PLIM

A 50:50 mixture of silica gel and bayerite was prepared in the presence of uranyl(VI) nitrate via batch sorption as highlighted in the methods. Silica in contact with alumina
powders tend to react. Part of the silica dissolves and adsorbs to the surface of the alumina powders, lowering the isoelectric point of the alumina.\textsuperscript{76} The mixture may be capable of identifying contributions from silica and or alumina sites by comparing the lifetimes resolved to the single mineral systems, thus aiding the identification of interactions of uranyl(VI) with the more complex and heterogeneous aluminosilicate clays.

The mixture at pH 4 was only weakly emissive requiring a binning factor of 9 affording approximately 3000 photons per trace. The PLIM data were modelled well to biexponential decays, with each time component split into at least two modal distributions (Fig. 5-19). From the image, it is fairly clear that the well-defined shape of the silica gel particles is no longer present. Indeed it appears the silica gel and bayerite have reacted; most likely the silica gel has reformed onto the surface of the bayerite powder.
Fig. 5-19: PLIM and lifetime distribution of uranyl(VI) bound to a 50:50 mixture of bayerite and silica gel at pH 3.83. The microscopy image (left) and associated lifetime distribution (right) are shown for both the first and second exponential terms ($\tau$), for more detail consult Fig. 5-7 caption.

The lifetimes resolved for the mixture at pH 4 are broad when compared to the single minerals. Although tenuous, it is possible to identify the large contribution in $\tau_1$ at $\sim$12 $\mu$s to silica gel and the lifetimes between 2 and 6 $\mu$s to bayerite. However an additional very long lifetime (above 80 $\mu$s) appears in the $\tau_2$ image. This interaction cannot be explained by considering the lifetimes of bayerite or silica gel alone, suggesting a combined interaction. However the positioning of the very long lifetimes somewhat
correlate with the silica gel interaction in $\tau_1$ at the same pH, suggesting that SiO bonds are involved in the interaction.

The mixture at pH 6 required two separate fits due to considerable differences in emission intensity. The central aggregate (Fig. 5-20) was found to contain mostly silica gel and the surrounding material was mostly bayerite, as indicated from a Raman microscope measurement of the same area (Fig. 5-22). Both the predominately bayerite area (Fig. 5-20) and silica area (Fig. 5-21) contain the presence of lifetimes comparable to silica gel at pH 6 or bayerite at pH 6. These are identified as blues in $\tau_1$ and reds in $\tau_2$, or reds in $\tau_1$, respectively. The remaining modal distribution at a lifetime value of ~140 $\mu$s correlates to neither single mineral. As seen with the pH 4 sample, this may indicate a combined aluminol and silanol interaction. This suggests that simple addition of two minerals that are important components in clays may not accurately model the combination of the individual components as initially anticipated.
Fig. 5-20: PLIM and lifetime distribution of uranyl(VI) bound to a 50:50 mixture of bayerite and silica gel at pH 6.09. Only the bayerite rich region is included in the model. The microscopy image (left) and associated lifetime distribution (right) are shown for both the first and second exponential terms (τ), for more detail consult Fig. 5-7 caption.
Fig. 5-21: PLIM and lifetime distribution of uranyl(VI) bound to a 50:50 mixture of bayerite and silica gel at pH 6.09. Only the silica rich central aggregate is included in the model. The microscopy image (left) and associated lifetime distribution (right) are shown for both the first and second exponential terms ($\tau$), for more detail consult Fig. 5-7 caption.
Fig. 5-22: Raman microscopy image of the same sample as studied by PLIM of the sample mixture at pH 6. Characteristic mineral shifts for bayerite and silica gel have been used to colour the image, blue representing the bayerite Raman shift at 550 cm$^{-1}$, and red indicating the D$_1$ Raman shift typically observed for silica gel. More detail is provided in the methods (chapter 2.5).

Interestingly, PLIM of uranyl(VI) sorbed to the mixture at pH 8 (Fig. 5-23) is more representative of bayerite than it is for silica gel, except that the precipitate observed at bayerite at the same pH has not formed at the mixture. Regardless, this indicates that the interaction with aluminol sites is more competitive than with the silanol at this pH. This is supported by literature data, which identifies an approximate AlO-H pK$_a$ of $\sim$7.5$^{,136}$ and a stronger more favourable interaction with aluminol over silanol in clay systems under similar conditions (see section 1.6.2 for a detailed discussion).
Fig. 5-23: PLIM and lifetime distribution of uranyl(VI) bound to a 50:50 mixture of bayerite and silica gel at pH 8.53. The microscopy image (left) and associated lifetime distribution (right) are shown for both the first and second exponential terms ($\tau$), for more detail consult Fig. 5-7 caption.

The mixture at pH 10 has a large silica gel aggregate which compares extremely well to the silica gel sample at the same pH (Fig. 5-24). It is unclear whether or not the same degree of lifetime shortening towards the edge of the aggregate is as significant in this sample, as it was for the silica gel only sample. The remainder of the image is almost drowned out in the extremely intense emission of the silica gel, but is also fit to a single exponential decay. Notably, this area does not correlate to bayerite or silica gel, but a combination of the two.
Fig. 5-24: PLIM and lifetime distribution of uranyl(VI) bound to a 50:50 mixture of bayerite and silica gel at pH 9.69. The image is fit to a single exponential but uses slightly different binning and background parameter due to large differences in intensity. The microscopy image (left) and associated lifetime distribution (right) are shown for both the first exponential terms ($\tau$), for more detail consult Fig. 5-7 caption.
Fig. 5-25: The lifetime distributions determined by PLIM of uranyl(VI) bound to a mixture of silica gel and bayerite (1:1 by weight) at pH 4, 6, 8 and 10. The x-axis is on a log\(_{10}\) scale to aid comparison, the y-scale is the number of pixels.

The distributions in lifetime for the PLIM of the two mixture samples at pH 4 and 6 is somewhat similar, this similarity in pH 4 and pH 6 (note the similarity in red and black lines in Fig. 5-25) is also observed for both the silica gel and bayerite only samples. Several more detailed similarities are drawn for each sample in turn, but generally, the majority of interactions can be explained by the consideration of the lifetimes of PLIM for the single minerals, but not all. This is important as it highlights that some modes of bonding from the uranyl(VI) equatorial plane may involve a combination of interactions that are provided by the intra-aggregate mixing of the two single minerals. The mixing may give rise to a third (or more) phase(s) that are not well described by the single minerals in turn. These may become important when considering the interaction of uranyl(VI) with the aluminosilicate clay mineral Stx-1b.

5.3.6 Uranyl(VI) sorbed to montmorillonite studied using PLIM

The Na-STx-1b montmorillonite is an opalinus clay and provides many more modes of interaction to uranyl(VI) than the silica gel, bayerite, or mixture samples. Its fundamental
structure is that of a 2:1 clay, providing edge interactions that may involve both silanol and/or aluminol groups, but other oxides present in the structure are also capable of partaking in bonding, namely MgO(H) and small amounts of TiO(H) or FeO(H). Bonding between these different oxides and the equatorial plane of uranyl(VI) is likely to have measurable effects on the uranyl(VI) lifetime values, in addition to the complexities observed with the SiO(H) (silica gel) and AlO(H) (bayerite) only samples. All the montmorillonite samples reported here were measured over a time window of 10 – 190 µs.

**Montmorillonite at pH 4** represents some of the challenges with fitting lifetimes to a diverse mineral surface. The PLIM in Fig. 5-26 shows an aggregate to the centre of the image that is more intense than the remainder of the image, pixels within this central aggregate are most suitably fit by a double exponential decay, whereas the remainder of the image forms a linear decay, indicating a single exponential model fit. Curiously, \( \tau_2 \) inside the central aggregate forms a broad lifetime distribution \( \sim 130 \) µs, very similar to that of the single exponential \( \tau_1 \) in the remainder of the PLIM window. Within the aggregate, \( \tau_1 \) is broadly fit to a value of 7 µs, similar to \( \tau_1 \) for the single component silica gel at the same pH. This would suggest that the aggregate is particularly opalinus and the remainder is much less so. The longer lived component that covers the image displays considerable clustering of lifetimes which deviate considerably around the mean (from \( \sim 90 \) to 180 µs). This is the first data in this series to have such a long lived lifetime at such a pH value (pH 4), suggesting that the interaction of uranyl(VI) with the surface is not with a single surface site as in silica gel or bayerite, but perhaps with the interlayer (although this would be unlikely, since most interlayer interactions have shorter lifetimes) or an inner-sphere interaction that has not yet been considered, with for example, a more protonated edge site interaction.
Fig. 5-26: PLIM and lifetime distribution of uranyl(VI) bound to STx-1b montmorillonite at pH 4.17. A double exponential is fit to the central aggregate and a single exponential to the remainder of the PLIM. For more detail consult Fig. 5-7 caption.
Montmorillonite at pH 6 required a binning factor of 4, affording ~3500 photons per trace. The PLIM data (see Fig. 5.27) were most accurately modelled by a double exponential decay. The distribution in the $\tau_1$ and $\tau_2$ is broad and the images display clustering of blues and reds (i.e. lifetimes of similar magnitude), suggesting at least two significantly different interactions. For example, in the top left of the image an area of ~15 µm$^2$ with a short uranyl(VI) lifetime value of ~2 µs, contrasts significantly with two areas, albeit of much smaller size (<5µm$^2$), with distinct lifetimes of 4 and 6 µs. These changes are the same across both $\tau_1$ and $\tau_2$, suggesting a change in the mineral environment (such as the local chemical composition) across the surface having a comparable effect on the two major uranyl(VI) species.

Fig. 5.27: PLIM and lifetime distribution of uranyl(VI) bound to STx-1b montmorillonite at pH 6.05. The microscopy image (left) and associated lifetime distribution (right) are
shown for both the first and second exponential terms (τ). For more detail consult Fig. 5-7 caption.

Montmorillonite at pH 8 required a binning factor of 5 affording ~4500 photons per trace. The distributions appear shifted to slightly higher values, but the lifetimes appear to follow similar trends as that of the pH 6 sample, displaying considerable heterogeneity at a local level. Unlike in the pH 6 sample, the effect of local environment does not have a consistent effect on the lifetime of components τ₁ and τ₂, affecting them to somewhat different extents (note that a comparison of colours in τ₁ and τ₂ do not always match, despite appearing to have similar distributions.

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**Fig. 5-28:** PLIM and lifetime distribution of uranyl(VI) bound to STx-1b montmorillonite at pH 8.01. The microscopy image (left) and associated lifetime distribution (right) are
shown for both the first and second exponential terms (τ). For more detail consult Fig. 5-7 caption.

Montmorillonite at pH 10 required a binning factor of 6 affording ~4000 photons per trace. As with the pH 4 and pH 8 samples, there appears to be certain aggregates of clay which give rise to certain lifetimes which are significantly different from those of the smaller aggregates. A clear distinction can be made in this case in the τ₁ lifetime distribution where the larger aggregate takes an approximate value of 10 µs, considerably longer than any of the lower pH montmorillonite samples. Then, the much smaller aggregates contribute to higher τ₁ lifetime values, forming a second mode in the distribution between 20 and 30 µs. τ₂ highlights considerable diversity between the smaller aggregates and with the appearance of lifetime values over 100 µs at various points across the PLIM.
Fig. 5-29: PLIM and lifetime distribution of uranyl(VI) bound to STx-1b montmorillonite at pH 9.64. The microscopy image (left) and associated lifetime distribution (right) are shown for both the first and second exponential terms ($\tau$). For more detail consult Fig. 5-7 caption.
**Fig. 5-30:** The lifetime distributions determined by PLIM of uranyl(VI) bound to montmorillonite at pH 4, 6, 8 and 10. x-axis is on a log$_{10}$ scale to aid comparison.

The lifetimes resolved for montmorillonite samples in these four samples demonstrate considerable heterogeneity and clearly include a multitude of interactions that are far more complex than the much simpler interactions of the single minerals silica gel and bayerite. However, more silica gel like interactions can occasionally be observed owed to similarities in the lifetime, for example an aggregate of clay is considered more opalinus than the surrounding clay owed to its inclusion of a second much shorter lived component for the sample at pH 4, the lifetime distribution of which matches well to silica gel at the same pH. It is not currently possible to assign every lifetime value which are observed for the very heterogenous nature of the interactions for uranyl(VI) bound to montmorillonite, especially for the pH 6 and pH 8 samples. These PLIM results serve to highlight the magnitude of the challenge of assigning the microscopic interactions of uranyl(VI) at these interfaces, and how oversimplified present modelling approaches may currently be.
5.4 Summary

The phosphorescence of uranyl(VI) sorbed to silica gel, bayerite and montmorillonite (Na-STx-1b) minerals has been studied using lifetime imaging for the first time. Batch sorption was performed in the absence of carbon dioxide and at low uranyl(VI) loading concentrations (4x10^-6 M [UO_2]; 10 g/L). Averaged lifetime data from PLIM measurements are comparable to bulk state lifetime measurements. However, heterogeneity within mineral aggregates is significant and easily becomes apparent even for simpler single mineral samples using PLIM. Micron sized deviations (i.e. changes in uranyl(VI) lifetime and hence bonding environment into micron-sized clusters) are observed in silica gel, resulting in bimodal distributions of the individual lifetime components, which have previously been thought to be normal distributed (i.e. unimodal). The diversity of uranyl(VI) speciation in bayerite samples is even more pronounced, with four and then five discernible uranyl(VI) species at pH 4 and 6 respectively, indicating at least two major binding modes or sites for bayerite under mildly acidic conditions, resulting in four distinctly separate lifetime groups.

A 1:1 (by weight) mixture of bayerite and silica gel demonstrates the complex chemistry that can be explained in part by consideration of the single mineral samples bayerite and silica gel. The PLIM of uranyl(VI) sorbed to montmorillonite demonstrates the extent of the complexity of defining speciation at this interface. At pH 4, PLIM is able to identify uranyl(VI)-mineral bonding across the sample that is most likely outer-sphere, in addition to stronger inner-sphere bonding to a silica rich aggregate within the bulk phase of the clay (i.e. it is interstitial). The pH 6, 8 and 10 samples display a broad and complex array of inner-sphere interactions. Some of the assignments are aided by comparison to single minerals, but others will represent bonding influenced by MgO(H), TiO(H), FeO(H) or another metal oxide. What is clear however, is the grouping of like interactions into aggregates of ~5-15 µm in diameter. All of this information is lost upon averaging the signal, as in a bulk state measurement, and this work clearly demonstrates the power of microscopic luminescence lifetime imaging to expose the extent of heterogeneity at the sub-micron level. This technique should find much future use in studying uranyl(VI) and by extension, other actinide ion mineral interactions at high spatial (~300 nm) and temporal (FLIM: ~ns or PLIM: <ms) resolution.
6 THESIS CONCLUSIONS

The future containment of nuclear waste depends on a thorough understanding of the interaction of radionuclides with the several engineered barriers of a GDF. This work has helped to address some of the most pressing environmental issues, namely the interaction of uranyl(VI) with aluminosilicate clay minerals.

The most significant findings of this research are the $log(K)$ values obtained in chapter 4. PARAFAC deconvolution of the 15 sample EEM data matrix (excluding non-trilinear data) was most suitably resolved using a 3-component model. The three components were represented by $\text{UO}_2$, $(\text{SiO})_2\text{UO}_2$ and $(\text{SiO})_2\text{UO}_2\text{OH}$, the luminescent properties for each were reported including the formation constants, $log(K)$, to a high degree of accuracy. A total of 350 Monte Carlo simulations were used to model the noise of the data, but no improvement to the overall fit was observed, increasing confidence in the original methodology. Raman spectra, which were used to observe the total symmetric stretching frequency of the $\text{UO}_6$ bond in the uranyl(VI) complexes, were compared to the same frequencies determined from the PARAFAC emission components, with reasonable correlation. This demonstrates that simple, inexpensive, luminescent measurements can be used to identify uranyl(VI) sorption species for a simple mineral system, using PARAFAC as a means of resolving the variance in the excitation and emission of the individual species, producing speciation detail to a high degree of accuracy.

The next most significant findings of this research are the new level of detail afforded from the phosphorescent lifetime image mapping (PLIM) measurements detailed in chapter 5. PLIM was used to study the sorption of uranyl(VI) to the minerals silica gel, bayerite, a 1:1 mixture of silica gel and bayerite and montmorillonite (STx-1b). It was observed that across the surface of a silica gel aggregate, sub-micron variation in luminescence lifetimes exists, and these were shown to be correlated to a change in the environment of the uranyl(VI) moiety and not a result of a variation in the intensity of emission. These microscopic variations become more apparent as intensity (and thus resolution) increases with increasing pH. At pH 10 the limit of the technique was demonstrated. PLIM of bayerite samples demonstrated the power of microscopy lifetime measurements by exposing the multi-modal nature of the single lifetime
components, in other words, it was shown that a single lifetime component $t_1$, may be represented by two or more discrete uranyl(VI) species. Popular bulk state spectroscopies such as XAS are frequently ambiguous, which is a result of the challenging characterisation of heterogeneous uranyl(VI) environments. This level of new detail is used to explain the close energetics of multiple edge-site species, changes in aqueous chemistry as well as some mild differences observed depending on the nature of the aggregation of the bayerite. PLIM of uranyl(VI) sorbed to montmorillonite (STx-1b) demonstrated that the surface is heterogeneous and that for a single sample, one area of the surface is more accurately modelled by a single exponential, whilst another area is more accurately modelled by a double exponential (Fig. 5-25). Some of the uranyl(VI) interactions with montmorillonite can be correlated to interactions with the single minerals silica gel and bayerite, but others will represent bonding influenced by MgO(H), TiO(H), FeO(H) or other metal oxides that were not present in the structures of the single minerals.

Important progress was made by the generation of a standardised luminescence measurement procedure, demonstrated in chapter 3, in order to obtain a broad dataset capable of exposing the general changes in surface interactions as a function of uranyl(VI) luminescence properties. The luminescence excitation ($\lambda_{em} = 520$ nm), emission ($\lambda_{ex} = 266$ nm, $\lambda_{ex} = 320$ nm or $\lambda_{ex} = 405$ nm), and lifetime ($\lambda_{ex} = 266$ nm, $\lambda_{ex} = 320$ nm or $\lambda_{ex} = 405$ nm and $\lambda_{em} = 520$ nm) properties for uranyl(VI) sorbed to silica gel and quartz; bayerite and boehmite; muscovite and kaolinite; STx-1b and SWy-2 montmorillonite at 77K have been collected and presented. It was found that a clear distinction between types of uranyl(VI) species bound to a silica surface were defined, namely between that of a crystalline silica and that of an amorphous silica. The quartz (crystalline) offers only bonding in a monodentate ($>\text{SiO}_2$) form, whilst silica gel (amorphous) only offers bonding in a bidentate ($>\text{SiO}_2$) form. The distinction is evidenced by the peak positions, which shift from an emission signal which is similar to other trimeric ligands (carbonate, phosphate) towards the red shifted emission that resemble the more flexible bidentate ligation of the two separate SiO-groups. Either formation leads to similar total symmetric stretching frequencies, as determined from the experimental emission spectra, This indicates similar stability for the overall
uranyl(VI) moiety, at least until the formation of the surface hydroxide complex, \((>\text{SiO})_2\text{UO}_2\text{OH}\), on silica gel only at pH >6, which has a slightly lower total symmetric vibrational stretching frequency and a red shifted emission signal. The luminescence properties of uranyl(VI) bound to aluminium hydroxide (bayerite) and to aluminium oxyhydroxide (boehmite) bear little resemblance to one another. The emission profile of uranyl(VI) with bayerite \((\text{Al(OH)}_3\)) is largely independent of pH and is described by two energetically similar inner-sphere complexes which form at edge- or corner-sharing sites. Speculation as to the nature of the uranyl(VI) species sorbed to boehmite \((\text{AlO(OH)})\) led to the identification of a pH dependent edge-site complex and a pH independent interaction with the surface plane. The sorption of uranyl(VI) to the sourced clay montmorillonites STx-1b (converted to Na-rich form) and SWy-2, demonstrated complex and diverse luminescence behaviour. The montmorillonite STx-1b displayed considerable similarity to the silica gel system, owed to its inclusion of a high concentration of semi-crystalline opal-CT. Beyond this, several uranyl(VI) interactions which display character representative of sorption to silanol \((>\text{SiO})\), aluminol \((>\text{AlO})\) or combined \((\text{Si-O-Al})\) sites were speculated. Based on the luminescence properties of uranyl(VI) bound to kaolinite and muscovite determined in this work, the speciation differs significantly to that reported in the literature, which has rarely identified sorption to silanol sites, but which were observed to be a significant contribution to the uranyl(VI) emission in this work. During the speciation assignment the most useful parameters were the peak positions and the total symmetric stretching vibrational frequency and the lifetime data were useful for describing trends that were not resolved by changes in the emission signal itself.

The most surprising results were the observation of a dependence of excitation energy on properties such as lifetime, or emission spectrum. This can only be a result of selective excitation. Analysis of the EEM data produced for the purposes of PARAFAC analysis in chapter 4 revealed that the excitation-emission relationship of uranyl(VI) luminescence is not trilinear. In other words, it was found that the position of peak centres in the emission spectrum of a 'single species' is dependent on the specific excitation energy, except for excitation into the energy continuum at 250 to 300 nm. This observation has not previously been reported and a detailed explanation is proposed.
in section 4.3.3 which considers the specific orientation of uranyl(VI) species with respect to the silica gel surface, resulting in preferential/selective excitation.

To conclude, this work has explored the luminescence properties of uranyl(VI) at the mineral water interface. Building on the current literature, several identifications have been made using bulk state luminescence measurements at liquid nitrogen temperature (77 K) and in the absence of carbonate for uranyl(VI) bound to silica gel, quartz, bayerite, boehmite, muscovite, kaolinite and montmorillonite. The project aims have been met: a reference dataset of low temperature luminescence measurements of uranyl(VI) bound to a wide range of minerals has been reported (chapter 3); PARAFAC has been applied and assessed for its suitability to deconvolute the sorption of uranyl(VI) to silica gel (chapter 4); and a methodology for and a thorough demonstration of the applicability of luminescence lifetime microscopy of uranyl(VI) at the mineral-water interface has been demonstrated (chapter 5).

### 6.1 Recommendations for future work

Two very useful technical developments have been demonstrated for an improved understanding of uranyl(VI) interactions with the water-mineral interfaces through this work. The first is the use of parallel factor analysis for the purpose of luminescence data deconvolution. Based on the success of the work here, it is reasonable to assume that for uranyl(VI) bound to other single minerals, as well as more complex clay minerals, the collection of EEM data, or perhaps TRLFS data, and subsequent deconvolution using PARAFAC will enable the identification of the underlying species responsible for the observed variation in luminescence. Secondly, the use of lifetime image mapping, a technique more commonly associated with the imaging of biological systems, can be applied to phosphorescent metals including uranyl(VI) with commercially available equipment.

This work does not consider the effect of biological material at the water-mineral interface. The most natural progression from this work towards a consideration of the complexities of microbiology would be to introduce organic material at the batch sorption stage, this may be done using humic acid. This, combined with the introduction of more mixtures of minerals and materials would provide a wealth of new interactions that would need to be observed and defined before approaching a soil type material,
complete with complex microbiology. The greatest concern will be quenching, for this, low temperature measurements have been shown to provide resolvable emission signals even from the most effective quenchers, for example uranyl(VI) carbonate complexes can be observed at cryogenic temperatures.\textsuperscript{50} I would anticipate that even liquid nitrogen temperatures would be sufficient to observe the vast majority of uranyl(VI) species that may be encountered under the most diverse environmental conditions. The next issue would be assignment, which is where the research conducted here would be of most benefit. Luminescence lifetime microscopy is able to resolve changes in the chemistry of uranyl(VI) for systems largely considered homogenous or simple. By lowering the temperature and gradually increasing the complexity of such measurements, combined with using a higher energy laser (i.e. Nd:YAG 4\textsuperscript{th} harmonic) and very long time windows (ms), I anticipate that this will afford a level of detail insofar unseen for the field. All of the components for such a set up are, fortunately, commercially available as they are routinely constructed for microbiology measurements.

The other major development arising from this work is the application of PARAFAC to EEM data from uranyl(VI) sorption. The results produce spectral components with high accuracy and reliability. Careful future experimental design, as demonstrated in this work, for more complex mineral systems will likely yield similar success. For example, one could measure not only the EEM but also the time-resolved response as a function of both excitation wavelength and emission wavelength. Doing this measurement for a series of samples, as demonstrated in this thesis, would produce 4-dimensional data, as opposed to the 3-dimensional data used here. The 4-way data is no more difficult to analyse using PARAFAC than the 3-way data and will almost certainly provide more detailed information, as well as providing more quantified lifetime elements for individual species, which are lacking in this field. Again I would recommend these sorts of experiments are conducted under very well controlled conditions and preferably at liquid nitrogen temperatures or below.
7 REFERENCES


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8 APPENDIX

8.1 XRD patterns and assignments

XRD patterns and assignments are presented in the following order:

- STX-1b (following Na-wash) (Fig. 8-1)
- SWy-2 (Fig. 8-2)
- Silica gel (Fig. 8-3)
- bayerite (Fig. 8-4)
- boehmite (Fig. 8-5)
- kaolinite (Fig. 8-6)
- muscovite (Fig. 8-7)
Fig. 8-1: XRD pattern of montmorillonite STx-1b
Fig. 8-2: XRD pattern of montmorillonite SWy-2
Fig. 8-3: XRD pattern of silica gel
Fig. 8-4: XRD pattern of synthetic bayerite
Fig. 8-5: XRD pattern of synthetic boehmite
Fig. 8-6: XRD pattern of kaolinite
Fig. 8-7: XRD pattern of muscovite
8.2 Lifetime values for chapter 4

The low temperature lifetime measurement parameters are tabulated, and presented in a quick reference format.

Table 8-1: The complete parameter set for all low temperature lifetime measurements. Sample code is [(pH)(mineral)]. All values are quoted to 2 decimal places except the lifetime values (in ns) which are to 0 decimal places. If a measurement is missing, it’s because it was not possible to resolve a luminescence decay.

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<th>y0 error (a.u.)</th>
<th>a1 value (a.u.)</th>
<th>a1 error (a.u.)</th>
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<th>τ1 error (ns)</th>
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Fig. 8-8: A quick reference bar chart of lifetime values ($\tau$) and associated error bars for all systems studied in chapter 4.
8.3 Additional information regarding FLIM/PLIM

8.3.1 Intensity images

Intensity images show where light is collected following a pulse of laser light, but disregards the time dimension. This is particularly useful for the FLIM of these mineral systems, as the intensity in the FLIM may indicate the extent of scatter from certain aggregates compared to others, indicating subtle changes in their morphology.

Fig. 8-9 and Fig. 8-10 are the intensity images for the samples at pH 4, the maximum intensity is set to 40 photons per pixel for both the FLIM and PLIM channel. The PLIM intensity is low and indicative of weak phosphorescence. Fig. 8-9 demonstrates the higher scatter from the crystalline bayerite sample, contrasted to the amorphous silica gel, which shows negligible scatter. The montmorillonite and mixture appear to scatter light to a similar degree. The mixture, which when observed through a visible microscope, showed signs of the two minerals, silica gel and bayerite, mixing at a particulate level (higher pH mixtures show evidence of mixing at an aggregate level), this mixing will be aided by the addition of HNO$_3$ during sorption.

![Fluorescence Intensity maps for mineral samples loaded with uranyl(VI) at pH 4](image)

*Fig. 8-9: FLIM intensity images for loaded mineral samples at pH 4. Each image is held to a maximum intensity of 40*
Fig. 8-10: PLIM intensity images for loaded mineral samples at pH 4. Each image is held to a maximum intensity of 40.

A combination of increased uranyl(VI) sorption and more luminescent species (i.e. longer lived), results in considerably more phosphorescence of the pH 6 samples than pH 4 samples. Fig. 8-11 shows the in focus bayerite aggregates as high scatterers, as well as dimmer slightly out of focus aggregates. Silica gel aggregates are visible as the highly phosphorescent uranyl(VI) is recorded in the FLIM image (due to incomplete relaxation), bright spots also appear but are absent from the PLIM channel (Fig. 8-12).

Fig. 8-11: Fluorescence intensity images for samples of bayerite, silica gel, montmorillonite and a mixture of silica gel and bayerite, loaded with uranyl(VI). Max intensity per pixel = 200.
Montmorillonite is more complex, the FLIM and PLIM are not correlated, i.e. There is no relationship between what gives rise to fluorescence or scatter, and phosphorescence of uranyl(VI)

The FLIM intensity images (Fig. 8-13) for samples at pH 8 are comparable to pH 4 samples except for silica gel, which appears bright in the FLIM due to the very long and very intense phosphorescence of the uranyl(VI). PLIM (Fig. 8-14) is dominated by the interaction of uranyl(VI) with silica gel, bright spots in the bayerite sample would suggest that uranyl(VI) has preferentially sorbed to certain aggregates, or that these species are much more intensely emissive. Several spots that are bright in the FLIM in montmorillonite and the mixture are not bright in the PLIM channel.
Samples at pH 10 sorb all of the uranium from solution (Table 5-2), as with lower pH samples, uranium bound to silica gives rise to the most intense emission. At pH 10 however, the intensity is extremely high.

**Fig. 8-15: FLIM intensity maps for samples at pH 10. Maximum intensity 40.**

**Fig. 8-16: PLIM intensity maps for samples at pH 10. Variable maximum intensities: Bayerite = 60; Silica = 3000; montmorillonite = 60; mixture = 200.**
The bayerite fluorescence (Fig. 8-15) indicates the amount of bayerite in the focus of the objective, which only approximately correlates with the phosphorescence. The silica gel fluorescence appears bright, but this is just the very long lived uranium phosphorescence being recorded in the FLIM channel due to incomplete relaxation. The montmorillonite sample contains several different aggregates with various fluorescent intensities which approximately correlate with the phosphorescence. The mixed sample clearly indicates a silica gel aggregate near some smaller bayerite aggregates. The bayerite may however have reacted with the silica gel as its PLIM intensity appears somewhat softer when compared to the bayerite only sample.

8.3.2 Blanks
Blank samples are prepared in the absence of uranium.

Light that is collected between 0 and 10 nanoseconds is captured by the FLIM channel, the presence of any sample in focus of the objective will collect more light compared to an absence of sample (i.e. increased background, or stray light) in the FLIM channel. The extent of fluorescence and scatter, and hence the intensity, can therefore be telling of the properties of the material. Amorphous materials scatter much less than crystalline materials. Bayerite is crystalline and silica gel is amorphous, whilst the montmorillonite clay contains both well order clay particles (crystalline) and opal (less-crystalline). The intensity of the FLIM can therefore be considered as a way to identify the local crystallinity of the material in the focus of the objective.

8.3.3 The goodness of fit
The distance between the collected data and the modelled regression line and is given by the $\chi^2_R$ (reduced chi-squared)

$$\chi^2_R = \frac{1}{n} \sum_{k=1}^{n} \frac{(N(t_k) - N_c(t_k))^2}{N(t_k)}$$

Where $N(t_k)$, $N_c(t_k)$, is the modelled and measured number of counts, respectively, at time $t_k$. $n$ is the number of data points. Equation (5) assumes that random error between the model and the data will follow a Gaussian distribution, it follows that a satisfactory fit of a lifetime map will conform to a Gaussian distribution about some value of $\chi^2$. 
Fig. 8-17: $\chi^2$ maps and $\chi^2$ distribution histograms of PLIM data for all samples loaded with uranyl(VI). Each image includes the distribution, which is fixed from 0 to 2.5, reds indicate values below 0.5 and blues indicate values above 2.0, which are considered outliers. The distribution also includes the mean as well as the mean plus or minus one standard deviation, to help illustrate the range of values. Columns and rows are grouped as indicated by the mineral and pH headers.

The models used to describe the PLIM data appear to be accurate for all systems except a few areas in the montmorillonite maps i.e. at pH 6 and 8, the bayerite at pH 6, and the mixture at pH 8 - indicated by blues.

### 8.3.4 Fitting FLIM

**Scatter.** The FLIM channel records photons detected between 0 and 10 ns, this includes a short period before and during the excitation pulse. Inelastic scatter, i.e. Raman scatter, may pass through the filter and enter the detector. However, scatter is observed in the detector as a spike in intensity with steep rise and decline times, which is clearly different to that of fluorescence. It follows that intense scatter cannot be fit by a decay model, an attempt to do so gives rise to a $\chi^2$ value considered outside of an acceptable range.
**Mineral fluorescence.** Fluorescent minerals in this context, will contain at least one fluorescent metal centre in an appropriate oxidation state. The lifetimes (and emission spectra) of these minerals vary considerably and are very sensitive to temperature.\(^{198}\) For example, aluminium oxy hydroxides, including bayerite, often display emission properties due to small quantities of \(\text{Cr}^{3+}\) substituting for \(\text{Al}^{3+}\) in the mineral lattice structure.[ref] Some key trends are observed, which help reflect the behaviour of the samples as the pH changes. Furthermore, the presence of the various phosphorescent uranyl(VI) species will influence the fluorescent properties of the mineral. Finally, these minerals are hydrated, which can further effect the fluorescent properties. This combination of factors creates a set of unique conditions, therefore it is variation in the values that will be of importance, not the values themselves.

Fig. 8-18: Fluorescent lifetime maps for all loaded samples fitted to a single exponential decay. Distribution histograms have been fixed at 500 to 3000 ps. Any fit outside of the chi\(^2\) range 0.5 to 2.5, or below a threshold value, is excluded from the distribution histogram and appears in black or white in the FLIM image.
**bayerite** appears to go through two phase transitions in the blank samples (Fig. 8-18), a species around 1.0 ns at pH 4, shifting to a higher value around 1.6 ns at pH 8, and then a third species at pH 10. pH 6 appears as a mixture of the pH 4 and pH 6 phases. This is not the case for the loaded samples, where all but the pH 6 sample conform to a bidentate distribution of lifetimes.

**silica gel** is not fluorescent. It gives very broad FLIM lifetimes, this is because the actual count of fluorescence is a product of phosphorescence.

**montmorillonite** pH 4 presents the most uniformly distributed FLIM, whilst 6 and 8 seem similar with several aggregates that appear to be different from one another. A significant phase change occurs at pH 10, splitting into a bidentate lifetime distribution.

**mixed** samples largely follow the trends observed for bayerite.

### 8.3.5 Input parameter tables

*Table 8-2: Table of input parameters for fitting FLIM of blank samples. Offset is set manually and is an average value from photons collected between T8 and T11 (Each pixel is represented by 256 T windows, or bins, over 10 ns, i.e. T=2.3 ps. The laser pulse, i.e. the IRF is observed at approximately T14 to T19, a decay is measured from T19). *value rounded from a representative pixel.*

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*Table 8-3:FLIM for loaded samples. FLIM for all samples are defined by a single incomplete exponential decay. *value rounded from a representative pixel.*

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