Structural and luminescent characterisation of uraniferous fluorapatite and haematite associated with phosphatic rocks of the Bijawar group in Sagar District, Madhya Pradesh (India)

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The structural and spectroscopic characteristics of phosphatic ferruginous shale samples from the Bijawar Group rocks from Sagar District of Madhya Pradesh (India) have been probed for identification of uranium species. Fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$, FAP) and haematite ($\alpha\text{-Fe}_2\text{O}_3$) were identified as the main phases in the separated mineral concentrates. The photoluminescence (PL) and X-ray absorption near edge spectroscopy (XANES) studies pointed to a strong experimental evidence of both U(IV) and U(VI) oxidation states in the mineral concentrate portion obtained from the same parent host rock. The PL spectrum has confirmed the charge transfer (f-d) transition bands in UV and near-UV regions with emission peaks at ca. 290, 313, 336, 399 and 416 nm, which has been attributed to the substitution of Ca^{2+} ions by U(IV) in FAP and broad structureless emission due to stabilisation of U(VI) as UO_6^{6-} in haematite. Time-resolved spectroscopy studies have revealed biexponential decay components lasting 2–5 ns for U(IV) species and 10 μs for U(VI) species. These characterisations revealed the fundamental information about the oxidation state and form of uranium in this region. Remediation measures for the Bijawar region are also suggested.

Keywords. Uranium; photoluminescence; X-ray absorption spectroscopy; X-ray diffraction.

1. Introduction

The need for nuclear self-sufficiency and the growing gap between energy demand and supply has necessitated the country to utilise modest (low

and intermediate) indigenous uranium reserves. Phosphate deposits are large potential sources of low-grade (0.005–0.020%) uranium reserves worldwide (Guzman *et al.* 1995). In India, the total reserve of rock phosphates is about 296.3 million

tons, which could serve as a significant secondary source of uranium. The Proterozoic Bijawar basin exposed along the southeastern margin of the Bundelkhand massif is an area of interest for uranium exploration associated with phosphatic rocks, which offers a substantial quantity of low-grade uranium (Banerjee *et al.* 1982; Roy *et al.* 2004; Dar *et al.* 2014a). The uranium mineralisation in the Bijawar basin is hosted by phosphatic ferruginous shale breccia and the average concentration of uranium varies approximately between 0.015% and 0.1%.

Previous structural and spectroscopic characterisation studies conducted in the Bijawar region and Palaeoproterozoic phosphorites of the Sonrai basin by X-ray diffraction (XRD), scanning electron microscopy (SEM) and inductively coupled plasma emission spectroscopy (ICP-AES) (Dar *et al.* 2014a, b) have focused on the determination of trace metallic constituents and phase analysis of the samples of this region; however, so far no report is available on the uranium species present in this region. The major analytic challenges in the speciation and spectroscopic characterisation of uranium species in the Bijawar region are their low concentration and interference due to the heterogeneous elements in the complex rock matrix. The present study is concerned with the characterisation and speciation of uranium in the Bijawar region.

An important key to understanding the uranium retention process (adsorption, precipitation or association with minerals) is to identify the uranium species. The mobilisation and deposition of uranium rely on its speciation which further depends on the geological, geochemical and hydrogeological process in the host environment. A basic understanding at the molecular level is required for understanding the uranium speciation. Hence, the techniques that can be used as a diagnostic tool at the molecular level such as luminescence spectroscopy, X-ray absorption spectroscopy (XAS) and Raman spectroscopy are employed.

In the present investigations, a comprehensive photoluminescence (PL) study along with lifetime decay by time-resolved photoluminescence (TRPL) has been performed on the sample from the Bijawar region to determine uranium oxidation states and the uranium moiety associated with these oxidation states. The PL results are further substantiated with structural, microstructural and spectroscopic characterisation performed using X-ray absorption near edge spectroscopy

(XANES), XRD, Raman spectroscopy, Fourier transform infrared (FTIR) spectra and SEM. The PL and XANES successfully identified the oxidation state and the uranium species associated with them instead of Raman, XRD and FTIR. This study aims to provide baseline information on the speciation of uranium in this region. The results of this study have been utilised to infer the state of uranium in the investigated mineral phase e.g., fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$, FAP) and haematite. Also, the data has been utilised to evaluate the remediation aspects of this region.

2. Geology

The Bijawar region is located in the Chattarpur district of Madhya Pradesh, India (figure 1). The Palaeoproterozoic metasedimentary rocks of the Bijawar Group resting upon the Archean Bundelkhand Basement Complex are overlain by the rocks of the Vindhyan Supergroup (Jha *et al.* 2012). The study area constituted the Proterozoic Bijawar basin spread over along the southeastern margin of the Bundelkhand massif. The northern margin of the basin is marked by an unconformity with different formations of the Bijawar Group predominantly comprising arenaceous with subordinate dolomitic units resting unconformably over the Bundelkhand Granite Gneiss. Along the southern margin of the basin, the Bijawar sediments are unconformably overlain by the middle Proterozoic clastic sediments of the Semri Group (Vindhyan). The uranium mineralisation in this area is hosted by ferruginous shale breccia with angular and subrounded fragments of quartz in the Lower Proterozoic Karri Ferruginous Formation (KFF) of upper Bijawar Group to the north of contact with Vindhyan sediments.

3. Methodology

The ferruginous shale sample SH-9 for structural and spectroscopic characterisation was collected from the Bijawar region during field season 2014–2015 during reconnaissance survey (24°20′52.5″N, 79°12′51″E). The SH-9 sample is a typical combination of FAP, iron oxides, hydroxides and oxyhydroxides along with cementitious silica, quartz and clay mineral. The optical microscopy and solid-state nuclear track detector (SSNTD) studies conducted on the sample have indicated Fe-rich material (haematite) and FAP as the main uranium-bearing radioactive phases

Figure 1. Geological map of the investigated area of the Bijawar basin.

(supplementary figure S1). The sample has clear partitioning available in the form of black and white portions constituting of FAP and haematite. The SH-9 was hence separated into FAP-bearing white portion called SH-9White (SH-9W) and haematite-bearing black portion hereby called SH-9Black (SH-9B). The representative subsamples of 100 g quantity from each of the lots, SH-9W and SH-9B, were powdered (mesh size -60) and homogenised by coning and quartering. The subsample from the homogenised lot was taken and the bulk uranium concentration in the samples was measured using NaI (Tl) gamma detector of size $5'' \times 4''$ with a multichannel analyser. The percentage of U_3O_8 content in SH-9W and SH-9B is identified to be 0.17% and 0.053%, respectively. In order to beneficiate the corresponding minerals, the samples were crushed to size ($0.15 \text{ mm} < \text{grain size} < 0.17 \text{ mm}$) and subjected to heavy liquid separation. The crushed samples were first subjected to bromoform separation (specific gravity, $\rho = 2.89 \text{ g/cm}^3$) to selectively concentrate the mineral species. The bromolight portion of the samples consisting of

quartz, mica and clay minerals was discarded and bromoheavy portion containing uranium species for both mineral concentrates was further subjected to methylene iodide ($\rho = 3.35 \text{ g/cm}^3$) separation. This mineral concentrate portion of both SH-9W and SH-9B was selected for the analysis. Phase purity and crystal structure of the mineral concentrate samples were identified by X-ray diffractometer using $\text{Cu K}\alpha_1$ radiation ($1.5406 \text{ \AA}$) fitted with a Ni filter in θ - 2θ mode (Rigaku). The data was collected from 20° to 70° with a step size of 0.02° . Simulation of crystal structure based on the measured XRD data was carried out using the refinement software. Surface morphology along with qualitative and semi-quantitative analysis of the fractured mineral was analysed with the field emission scanning electron microscope (Carl-Zeiss, SUPRA 40) equipped with X-ray energy dispersive spectroscopy. Raman spectra were obtained using a Raman spectrometer with an excitation source of 785 nm with spectral resolution of 1 cm^{-1} (Renishaw inVia). Infrared absorption spectra were taken in the range 400 – 4000 cm^{-1} using FTIR using the standard KBr technique

(Perkin-Elmer). The optical absorption was measured in the spectral range 190–700 nm using UV–Vis–NIR spectrometer (UV 3101 PC Shimadzu). The photoluminescence (PL and PLE) spectra were measured using an FLS920 fluorescence spectrometer (Edinburgh Instruments Ltd.). For excitation, a 450 W ozone-free xenon arc lamp has been used as a standard light source. TRPL measurements in the nanosecond and microsecond decay scales were performed by nanosecond (ns) pulse diode laser ($\lambda_{\text{exc}} = 285$ nm, pulse duration 750 ps and repetition frequency 5 MHz) and a xenon microsecond (μs) flash lamp using the FLS920 lifetime spectrometer (Edinburgh Instruments Ltd.). XANES spectra of the samples were recorded in fluorescence mode at U L_{III} -edge (17,116 eV) and those standards were taken in transmission mode using the vortex energy detector at BL-9, scanning X-ray absorption fluorescence spectroscopy beamline of INDUS-2 synchrotron source (2.5 GeV, 100 mA) at Raja Ramanna Center for Advanced Technology (RRCAT), Indore.

4. Results and discussion

The structural and spectroscopic characterisation pertaining to SH-9W (FAP) and SH-9B (haematite) is discussed below.

4.1 X-ray diffraction

4.1.1 Fluorapatite

The qualitative analysis of the XRD revealed FAP to be the main phase of SH-9W (figure 2a). The intense 2θ reflections at 25.89° , 29.01° , 31.90° , 32.20° , 33.10° , 34.16° , 39.94° , 46.87° , 49.57° and 51.41° corresponding to the hkl planes (002), (120), (121), (112), (300), (202), (310), (222), (123) and (410), respectively, were observed in agreement with the previous literature (JCPDS #15-0876). Additional reflections corresponding to calcite were observed at 46° , 54° (JCPDS # 05-0586) and at 24° corresponding to haematite (JCPDS #33-0664). The structure of FAP is a hexagonal belonging to the space group $P6_3/m$ with unit cell

Figure 2. Structural characterisation of SH-9W and SH-9B showing the vibrational and structural information. The measured XRD patterns of (a) SH-9W showing predominantly FAP bands (the inset shows the schematic representation of the hexagonal structure of FAP with Ca atoms in green coordinated to phosphate tetrahedra in red and fluorine atoms in white) and (b) SH-9B (the inset shows the schematic representation of the corundum structure of Fe_2O_3 . The face-sharing and edge-sharing FeO_6 octahedra are shown to be stacked parallel to the c -axis; $2/3$ of the octahedral sites are occupied by Fe^{3+} atoms. The red and blue spheres represent iron and oxygen, respectively). The figures shown are the orthographic views. (c) Raman spectra of SH-9W showing mainly the FAP bands, (d) Raman spectra of SH-9B, (e) FTIR pattern of SH-9W and (f) FTIR pattern of SH-9B.

dimensions of $a = b = 9.367 \text{ \AA}$, $c = 6.884 \text{ \AA}$ and cell volume of $519.77 \text{ \AA}^3$. The crystal refinement of the recorded XRD pattern was carried out by considering only the pure FAP phase free from other impurities. The experimental XRD patterns were simulated to obtain the lattice parameters $a = 9.397 \text{ \AA}$, $c = 6.878 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 120^\circ$, lattice volume $V = 525.96 \text{ \AA}^3$ and space group $P6_3/m$. The relatively weak agreement was observed between the experimental and simulated structure (weighted residual error, $R_{\text{wp}} = 24\%$) due to the presence of impurity phases. The different crystallographic sites of FAP can accommodate a variety of rare earth elements (REE) and radionuclides; therefore, one possible explanation may be due to the occupancy of the Ca(I) and Ca(II) sites by rare earth dopants (Nary Szabo 1930; Hughson and SenGupta 1964; Kay *et al.* 1964; Cockbain and Smith 1967; Mackie *et al.* 1972; Gunawardane *et al.* 1982).

The structure of FAP has been well reported in the literature (Nary Szabo 1930; Beevers and McIntyre 1946; White and Zhili 2003). The unit cell of FAP comprises 42 atoms with 4Ca(1), 5Ca(2), 6(PO₄) and 2F atoms. There are two crystallographically inequivalent Ca sites, Ca(I) and Ca(II), having a relative ratio of 60:40 and three inequivalent O atoms, a tetrahedral oxyanion PO₄³⁻ and a chain of fluorine along the *c*-axis. The point group symmetry of the Ca(I) site is C_3 , with each Ca having six oxygen nearest neighbours that form a distorted triangular prism about the Ca²⁺ ion. The Ca(II) site has C_s symmetry with the Ca²⁺ ions sitting at the corners of equilateral triangles with an F ion in the centre. The hexagonal bipyramidal structure of FAP having non-centrosymmetric space group $P6_3/m$ has been shown in the inset of figure 2(a). No distinct peaks corresponding to any uranium mineral were obtained indicating that uranium has been substituted at the lattice site rather than at the interstitial site.

4.1.2 Haematite

The XRD pattern of SH-9B (figure 2b) showed intense 2θ reflections at 24.23° , 33.19° , 35.79° , 40.89° , 54.19° , 62.47° and 64.11° corresponding to (012), (104), (110), (113), (116), (214) and (300) *hkl* planes, respectively, indicating haematite to be the main phase (JCPDS # 33-0664). The crystallographic parameters identified are structure: hexagonal; space group: $R3C$; lattice parameters

$a = 5.032 \text{ \AA}$, $b = 5.032 \text{ \AA}$, $c = 13.76 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 120^\circ$ and $V = 301.78 \text{ \AA}^3$ which are close to the values reported in the literature of pure haematite phase $a = b = 5.038 \text{ \AA}$, $c = 13.77 \text{ \AA}$, $V = 302.72 \text{ \AA}^3$ (Pauling and Henricks 1925; Willis and Rooksby 1952). Small ($R_{\text{wp}} = 13\%$) values of the structure refinement in the case of SH-9B suggest that the simulated XRD pattern agrees well with the measured XRD pattern and no impurity phases are observed within the detection limit of XRD.

4.2 Raman spectroscopy

Raman spectroscopy is a powerful tool to study the structural and vibrational property of a material that gives the useful information about cationic substitution and different phases (Jorge Villar *et al.* 2005). It can be used to study the submicron grain sizes of uranium species.

4.2.1 Fluorapatite

Raman spectra of samples SH-9W are shown in figure 2(c). The modes corresponding to the stretching, translational and internal vibration modes of the PO₄ groups are visible in the spectra. A strong band is observed at 964 cm^{-1} characteristic of the ν_1 asymmetric stretching of the PO₄ group while the bands at 1058 and 1083 correspond to PO₄ ν_3 anti-symmetric stretching band and those at 403 and 439 to ν_2 anti-symmetric stretching band (Comodi *et al.* 2001). However, no bands corresponding to the uranium species were visible.

4.2.2 Haematite

In the case of SH-9B (figure 2d) the representative bands of haematite are observed at 291, 232, 410, 493, 618 and 1322 cm^{-1} which are consistent with the XRD results (Hanesch 2009). The Raman spectral peak of haematite corresponds to a well-crystallised structure. The bands corresponding to 657 cm^{-1} indicated the presence of small amount of lepidocrocite ($\gamma\text{-FeOOH}$). Haematite is a mineral formed by weathering process in the soils, hence there is a high possibility of it being present along with iron oxides such as lepidocrocite ($\gamma\text{-FeOOH}$) or goethite ($\alpha\text{-FeOOH}$).

4.3 FTIR spectroscopy

The FTIR spectrum was used to determine the nature of functional groups which could possibly influence the adsorption of the uranium in the samples.

4.3.1 Fluorapatite

The FTIR spectra of SH-9W mainly demonstrated the vibrational modes for PO_4^{3-} and CO_3^{2-} in the FAP (figure 2e). Peaks at 470, 573, 601, 964, 1056, 1093 cm^{-1} are characteristic bands of the PO_4 group (Stoch *et al.* 1997). The P–O stretching has been observed at 960 cm^{-1} and O–P–O bending is observed at 470 cm^{-1} , respectively. The other important characteristic peak of PO_4 tetrahedral groups was the P–O stretching ν_3 vibration mode, which was visible at 1056 and 1093 cm^{-1} . The bands at 572 and 601 cm^{-1} are the ν_4 vibration mode of the phosphate group. In addition, a doublet appears at 1429 and 1490 cm^{-1} corresponding to the ν_3 vibration mode and the band centred at 869 cm^{-1} for ν_2 vibration mode of the carbonated groups. The peaks at 1999 and 2088 may be due to PO_4^{3-} overtones (Azami *et al.* 2011).

4.3.2 Haematite

Figure 2(f) revealed the vibrational spectra of SH-9B. The spectra revealed the characteristic bands of haematite between 470 and 550 cm^{-1} and are in agreement with past studies (Betancur *et al.* 2012). The other bands at 946 and 1056 cm^{-1} are due to symmetric stretching bands of the PO_4 group due to the impurity phase of FAP in it. The presence of bands at 1632 cm^{-1} indicates ν_2 bending modes of water, which proves structurally inequivalent water molecules in the crystal structure.

These characterisations confirm that SH-9W and SH-9B largely consist of FAP and haematite, and no signature of uranium species was evident.

4.4 Surface morphology studies

4.4.1 Fluorapatite

Figure 3(a) demonstrated the SEM image of SH-9W and it has been concluded that these crystals are dense euhedral crystals of hexagonal FAP formed due to homogeneous or heterogeneous crystallisations. Semi-quantitative analysis using

Energy Dispersive X-ray (EDX) revealed the Ca/P ratio of 1.76 in FAP.

4.4.2 Haematite

Figure 3(b) represented the rounded grains of haematite in SH-9B at 300 nm scale similar to that reported in the literature (Chung *et al.* 2014). The grain size appeared to be uniform and low porosity was visible indicating a well-crystallised structure.

Figure 3(c and d) indicates the SEM observations in backscattered (BSE) mode of SH-9 bulk sample revealing the presence of FAP, kaolinite and haematite at 300 μm resolution. The measurements through BSE (EDX) revealed the presence of Fe, Ca, P along with the high concentration of rare earth ions; Eu, Dy, Ce and transition metal elements such as Mn, Mg and actinides such as U and Th.

4.5 PL studies

Luminescence spectroscopy is an ideal diagnostic tool for speciation of uranium when compared to other techniques such as XRD, electron paramagnetic resonance, Raman and chemical analysis due to its high sensitivity, specificity, simplicity, ease of operation and quick response (Morris *et al.* 1996; Catalano *et al.* 2004; Krepelova *et al.* 2007; Regensperg *et al.* 2010; Reitz *et al.* 2011; Baumann *et al.* 2012; Jones *et al.* 2015).

The difference in the spectral luminescence of U(IV) and U(VI) species helps in their detection and discrimination in the complex rock matrix. The PL studies were therefore conducted to identify different uranium species. The absorption spectrum of SH-9 sample is indicated in figure 4(a). SH-9 was excited by UV–Vis light corresponding to the basic and activated electronic and vibronic level of uranium and emission was monitored in the range 250–700 nm. The absorption spectra exhibited a relatively broad and smeared out transition in the range 33,000–45,000 cm^{-1} without any distinct spectral peaks due to the greater radial overlap of 5f orbitals. These broad band features in the absorption spectra indicated the interconfigurational transitions between the $5f^2$ (ground state of uranium) and 5f 6d states, namely f–d transitions that occur in energy above 27,000 cm^{-1} . The intense absorption spectra corresponding to the lowest energy level is observed at 230 nm (43,478 cm^{-1}), which is 15,000 cm^{-1} lower than that of

Figure 3. SEM micrograph of (a) magnified view of SH-9W, (b) magnified view of SH-9B, (c) the SEM micrograph, in BSE mode, of the whole rock sample of SH-9 (the arrow leads to the EDX spectrum revealing the presence of Eu, Dy, Na and Si within the material). (d) The SEM micrograph in BSE mode of the uranium adsorbed on kaolinite (the arrow leads to the EDX spectrum revealing the presence of actinides, U and Th).

free U(V), (U^{4+}) ion since the lowest f–d transition corresponding to U(V) is placed at $59,183\text{ cm}^{-1}$. The optical band gap of the sample was determined to be 4.5 eV.

4.5.1 Fluorapatite

Figure 5(a) shows the room temperature emission spectrum of SH-9W under excitation at 245 nm. The spectral length was limited to 450 nm to avoid second-order diffraction peak due to the excitation wavelength. The deconvolution of the emission spectra revealed sharp peaks at 290, 313, 348 and 399 nm.

The spectral effects could be explained by the 5f–6d orbital hybridisation of uranium under the influence of crystal field. Several other studies have also reported the similar luminescence of U(IV) and U(III) covalent compounds in different crystal field symmetry and matrices; U^{4+} in Cs_2UCl_6 (O_h symmetry) (Satten *et al.* 1965), U^{4+} in UCl_4 and $ThCl_4$ (D_{2d} symmetry) (Malek *et al.* 1984), $[Li(THF)_4][UCl_5(THF)]$ (C_{4v} symmetry) (Hashem *et al.* 2013), U^{4+} in UF_4 (Carnell *et al.* 1991), U^{4+} doped $LiYF_4$ single crystal (Godbole *et al.* 2001), U^{4+} doped into YF_3 single crystal (Kirm *et al.* 2003) and sulphate complexes in a frozen matrix (Görller-Walrand *et al.*

1993). The luminescence of uranium in natural apatites with ca. 308 nm peak and emission in the wavelength range of 400–800 nm were observed by Panczer *et al.* (1998).

Uranium has a ground state electronic configuration of $5f^36d^17s^2$. Uranium (V) has two unpaired electrons in the 5f state and electronic ground state of uranium is 3H_4 . These emission spectra might be assigned to either excitation into a band of f–d and ligand to metal charge transfer character followed by energy transfer from the 5f–6d electronic configurations to envelopes of states arising from the ground state $5f^2$ configuration or due to the f–f transitions from 1S_0 to lower 5f levels of uranium (Hashem *et al.* 2013). Both these intraconfigurational f–f transitions and interconfigurational charge transfer transition occur in the similar time span. However, the characteristic excitation band corresponding to the emission at ca. 313 nm is quite broad (figure 4b) and the excitation wavelength is observed at 230 nm which corresponds to $5f^2$ – $5f6d$ transition (Kirishima *et al.* 2004). The interconfigurational $5f^16d$ – $5f$ transitions are parity allowed unlike $5f$ – $5f$ transitions which are parity forbidden. They are characterised by short emission lifetimes and emission bands of high intensity located in the UV range. Radiative transitions from $5f6d$ to 3H_5 , 3F_3 , 3H_6 and 3P_0

Figure 4. (a) UV-vis-NIR spectra of SH-9 showing the overlap of charge transfer band due to $5f^2-5f6d$ and oxygen $2p$ to uranium $6d$ orbitals. (b) PL excitation of SH-9W (detector at 313 nm), (c) PL excitation of SH-9B (detector at 470 nm) and (d) PL excitation of SH-9 while keeping the detector at 590 nm showing the characteristic excitation peak of Eu.

resulted in emission peaks at ca. 290, 313, 348 and 399 nm. The positions of the energetic bands are dependent on the coordination environment, crystal field symmetry and the excitation wavelength of the material. Figure 6 shows the band energy diagram of U^{4+} ion (Kirishima *et al.* 2004).

With regard to the crystal field, the two calcium positions of FAP have different stereochemistry and are able to accommodate a variety of monovalent (Na^+ , K^+), divalent (Sr^{2+} , Pb^{2+} , Ba^{2+} , Mn^{2+} and Cd^{2+}), trivalent rare earth element (REE^{3+}) and tetravalent actinide (Th^{4+} and U^{4+}) cations (Luo *et al.* 2009). The Ca site occupancy of rare earth and the actinide substituted FAP ions is controlled by the bond valence, charge compensation mechanism and the radius constraints. The Ca(I) (effective radius 1.18 Å) site at the

4f Wyckoff position is described as having coordinated to nine oxygen atoms with point group symmetry C_3 , whereas the Ca(II) sites in the 6 h Wyckoff positions (effective radius 1.06 Å) are eight coordinated to seven O atoms and one F atom having C_s symmetry (Elliott *et al.* 2002). According to Shannon (1976), the U(IV) in FAP having nine-fold coordination (effective radius 1.05 Å) substitutes at the Ca(II) position. The charge imbalance created by the substitution of higher valent U^{4+} is compensated by the coupled substitution involving Na^+ , Si^{4+} and vacancies (Elliott 1994). The compositional analysis of the samples in the EDX spectrum indicates the presence of both Si and Na in SH-9W and SH-9B (figure 3c and d). So, the local charge compensation may be maintained by the following coupled substitution in SH-9W:

Figure 5. Photoluminescence emission spectra showing $5f6d-5f^2$ transitions of (a) SH-9W ($\lambda_{exc} = 245$ nm) and (b) SH-9W ($\lambda_{exc} = 285$ nm). The left inset shows the $f-f$ transition corresponding to U^{4+} ion, while the right inset indicates the emission spectra due to UO_6^{6-} ion. (c) Photoluminescence emission spectrum showing $5f6d-5f^2$ transitions of SH-9W ($\lambda_{exc} = 350$ nm). The right inset indicates transitions at 620, 669 and 578 nm due to Eu^{3+} and Dy^{3+} ions. Photoluminescence emission spectrum showing $5f6d-5f^2$ transitions of (d) SH-9B ($\lambda_{exc} = 245$ nm), (e) SH-9B ($\lambda_{exc} = 285$ nm), and (f) SH-9B ($\lambda_{exc} = 350$ nm) excitation.

Figure 6. Band energy diagram of the U^{4+} ion.

The emission spectra of SH-9W on being excited by 285 and 350 nm are shown in figure 5(b and c), respectively.

The spectra of SH-9W under 285 nm excitation with a xenon lamp and filter at 335 nm can be deconvoluted into two structured emissions in the range 300–450 and 450–500 nm (figure 5b). The transitions at 313 nm ($5f^16d^1-^3F_3$), 319 nm ($5f^16d^1-^3F_4$), 348 nm ($5f^16d^1-^3H_6$), 409 nm ($5f^16d^1-^1D_2$) and 448 nm ($5f^16d^1-^3P_1$) are attributed to the signature of U^{4+} as discussed above and an inhomogeneously broadened and smeared out emission spectrum without any band resolution in the spectral range 450–500 nm was observed. The second component of the emission spectra is similar to that exhibited by uranium in the hexavalent state U(VI). In the hexavalent state, uranium can exist as $(UO_2)^{2+}$ or U(VI) in tetrahedral coordination: $(UO_4)^{2-}$ or uranium in octahedral

coordination: $(UO_6)^{6-}$. While $(UO_4)^{2-}$ emits in the orange-red region, both UO_2^{2+} and octahedral UO_6^{6-} emit in the green region. Both these uranyl and uranate emissions are electric dipole parity-forbidden transitions; however, UO_2^{2+} emission can be distinguished from that of the latter on the basis of its characteristic vibronic structure exhibiting a set of equidistant lines. The absence of vibronic structure clearly indicated that the transition intensity is from the electronic origin due to substantial electric dipole change during the electronic excitation at the low-symmetry site indicating the fact that the luminescence is from the uranate group. This is similar to the transition observed by U: $SrZrO_3$ and U: SrB_4O_7 (Tanner *et al.* 1997). The origin of this emission is assigned to the parity-forbidden charge transfer transition $5f-t_{1u}$ that is vibronically coupled to ungerade vibrational modes of the UO_6^{6-} octahedron. The U(VI) may be present either as a substitution of Ca atom in FAP by U^{6+} or being adsorbed on Fe(III) as a uranate ion. In seven-fold coordination, considering the ionic radii of Ca^{2+} and U^{6+} (0.76 Å), it was concluded that uranium mainly substituted at the Ca(II) position. The charge compensation in the case of U^{6+} substitution in FAP takes place according to the following formula:

On excitation with 350 nm laser, two spectral components arise from three chemically different species in SH-9W (figure 5c). The mathematical fit to the emission decay curve for the first component signified peaks at 329, 386, 413 and 436 nm which are attributed to U^{4+} to that observed in the case of 245 nm. The second component signified intense emission of red colour in the range 550–700 nm. These strong emissions at 578, 620 and 660 nm could be attributed to rare earth ions. The PL of rare earth ions originates from the electronic transitions in the 4f orbitals and the wavelength is independent of the host lattice. Fleet and Pan (1995) have noted that the structural role of REE in apatite remains unknown, as a given REE may be distributed over both the Ca sites. Further, Hughes *et al.* (1991) suggested that La to Pr ions should prefer the low-symmetry Ca(II) position, whereas Pm to Sm should occupy the Ca(I) position. The red emission at 620 and 669 nm is related to the electronic radiative $^5D_0-^7F_j$

($j = 1, 2, 3, 4$) transition of the Eu^{3+} ions. This electric dipole radiation is otherwise forbidden by the Laporte selection rule. However, the transitions become permissible for Eu^{3+} occupancy at the C_s non-centrosymmetric site. The luminescence of Eu substituted apatite has been widely studied by Blasse (1975) and Gaft *et al.* (2001) and it has been observed that Eu^{3+} ions doped in apatite occupy mainly Ca(II) sites (Wright *et al.* 1995). The REE data performed using the ICP-AES analysis revealed the corresponding values (La: 8 ppm; Ce: 15 ppm; Pr: <5 ppm; Nd: 7 ppm; Sm: 3 ppm; Eu: 0.8 ppm; Gd: 4 ppm; Tb < 2 ppm; Dy: 3 ppm; Ho < 1 ppm; Er: 2 ppm; Tm < 0.5 ppm; Yb: 1.4 ppm; Lu < 0.5 ppm; Y: 26 ppm). This was further confirmed by the observation of 578 nm (5D_0 – 7F_0) transition observed under 396 nm excitation. The emission peak at ca. 578 nm is due to the transition of Dy^{3+} between $^4F_{9/2}$ and $^6H_{13/2}$ and is connected with Dy^{3+} in the Ca(II) site. Intense luminescence of this line is associated with the lower symmetry of the site.

Although XANES measurements have indicated U(IV) state for SH-9W, PL measurements have indicated both U(IV) and U(VI) states for both the samples which are due to the higher sensitivity of PL when compared to XANES.

Figure 4(b) showed the excitation spectra of SH-9W corresponding to the emission bands at 313, 336, and 400 nm. The excitation spectra corresponds to the broad band extending from 190 to 250 nm. The excitation spectra due to the emission at 470 nm (figure 4c) also revealed the similar features. Hence, the excitation spectra can be explained due to the charge transfer transition from oxygen (2p) to uranium (6d) orbitals.

4.5.2 Haematite

Figure 5(d) shows the PL emission spectrum of SH-9B in the range 250–450 nm at an excitation of 245 nm. The feeble emission peaks in the near UV region are due to the impurity phase of FAP in SH-9B. The emission spectra noted at 285 nm excitation by keeping a filter at 335 nm revealed a structureless emission at 470 nm (figure 5e). As we have discussed earlier, from the nature of the luminescence, this uranium moiety could be attributed to uranate $(\text{UO}_6)^{6-}$ ion. Since SH-9B majorly consists of haematite and other iron oxy(hydro) oxides, goethite and lepidocrocite are known to be effective at reducing the mobility of U(VI) through either their

high adsorption capacity (surface adsorption) or, where Fe(II) is present, via reductive precipitation to poorly soluble U(IV) phase (Hsi and Langmuir 1985; Dzombak and Morel 1990; Waite *et al.* 1994; Finch and Murakami 1999; Dodge *et al.* 2002), hence the $(\text{UO}_6)^{6-}$ ion may be either adsorbed or substituted at the structure. Earlier studies by Duff and Massey have observed uranium coprecipitation with iron oxides with the incorporation of a uranate species (U^{6+}) in the haematite structure (Duff *et al.* 2002; Elton *et al.* 2012; Massey *et al.* 2014). U(VI) (ionic radius = 0.870 Å) substitutes for Fe(III) (ionic radius = 0.785 Å) in octahedral sites and charge compensation is achieved through protonation/deprotonation of nearby hydroxyls, or the introduction of structural vacancies at cation sites hence it is contemplated that $(\text{UO}_6)^{6-}$ ion has substituted at the Fe(III) site in the haematite structure.

The origin of emissions at 611 and 669 nm on excitation with 350 nm in SH-9B (figure 5f) of transitions is due to the presence of Eu ions present in FAP at lower symmetry site C_s . The excitation spectra of SH-9 while keeping the detector at 590 nm revealed the characteristic f–f transition corresponding to the 7F_0 – 5L_6 transition of Eu^{3+} ions (figure 4d). PL emission indicated the presence of U(IV) and U(VI) species apart from the rare earth ions.

4.6 Time-resolved photoluminescence

4.6.1 Fluorapatite

The TRPL decay curves of SH-9W at 313 and 336 nm and that of SH-9B at 470 nm are shown in figure 7(a–c), respectively. We note that the lifetimes are biexponential components when deconvolution of the data is employed giving lifetime values in the range of 2–10 ns. The decay curves were fitted with a biexponential function using the equation where A_1 and A_2 are pre-exponential factors and τ_1 and τ_2 stand for the lifetime of fast and slow decays, respectively. The observed effective lifetime τ for biexponential decays for SH-9W is $\tau_1 = 2.04 \pm 0.014$ ns (67%) and $\tau_2 = 0.43 \pm 0.002$ ns (34%) at 313 nm; $\tau_1 = 4.19 \pm 0.022$ ns (70%) and $\tau_2 = 0.64 \pm 0.008$ ns (30%) at 336 nm typical of U(IV) species. For U(IV) species, multi-exponential decays hinting at complex deactivation or multiple excited states have already been observed (Hashem *et al.* 2013). However, we have observed the biexponential decay indicating the presence of two distinct U(IV) species. This biexponential decay could

Figure 7. TRPL decay profile of (a) SH-9W at 313 nm emission (the inset shows the lifetime data and the parameters generated by exponential fitting), (b) at 336 nm emission, (c) at 470 nm emission (all the spectra were acquired at 285 nm excitation).

have arisen due to the stabilisation of U(IV) in two coordination environments; either Ca(I) in seven-fold coordination or Ca(II) in nine-fold coordination.

4.6.2 Haematite

The decay measurements of SH-9B at 470 nm (figure 7c) revealed two different decay times in the range of μs , characteristic of uranate ion. The lifetime values obtained are 10.49 μs (69%) and 1.12 μs (31%). The uranium in uranyl form has a lifetime in the range of 100s of μs ; however, in the present case the lifetime has clearly indicated that the uranium is present as a uranate ion.

4.7 $U_{L_{III}}$ -edge XANES analysis

XAS containing XANES has become a well-established tool for oxidation state determination of actinides. XANES has been carried out on SH-9W and SH-9B uranium L_{III} edge absorption in the fluorescence mode. The calibration for energy was performed by measuring the edges of the natural reference samples; Rutherfordine (UO_2CO_3) for U(VI) and uraninite (UO_2) for U(IV), the inflection points of which were obtained at 17,168.2 and 17,165.3 eV, respectively.

4.7.1 Fluorapatite

In the case of the spectra for SH-9W, U L_{III} -edge edge jump position (eV) is obtained at 17,163.9 eV indicating that uranium in FAP-rich portion is present in the tetravalent state, U(IV) state, which implies that either U^{4+} has substituted Ca^{2+} ions (figure 8a).

4.7.2 Haematite

The U L_{III} -edge jump position (eV) for SH-9B has been obtained at 17,167.9 eV which is similar to UO_2CO_3 standard, revealing that SH-9B has U(VI) oxidation state (figure 8b). Around the post-edge region, multiple resonance features such as a 'shoulder' are usually observed in U(VI) XANES spectra. This feature is often attributed to the structural coordination environment around the U(VI) atom, which usually exists as the dioxo linear moiety (a UO_2^{2+} ion group). Most U(VI) solids and solution species have a coordination number (CN) of 6–8 (Weigel 1986; Burns *et al.* 1996; Duff *et al.* 2000), whereas U(IV) in $\text{UO}_2(\text{s})$, e.g., usually has a CN of eight or nine, and does not have a 'shoulder'. Since XANES spectra of SH-9B have a very similar shoulder at the post-edge side as UO_2CO_3 XANES standard of U(VI) which indicated that uranium has the possible local coordination of octahedral or close to it. However, the

Figure 8. (a) U L_{III}-edge XANES spectra of 4+, 6+ and SH-9W, SH-9B samples and (b) first derivative of XANES spectra.

studies have suggested that U(VI) in the form of UO_6^{6-} replaces the Fe^{3+} ion.

Mössbauer studies conducted on the above sample have indicated the presence of Fe in Fe(III) oxidation state which indirectly points to the presence of uranium in the hexavalent form since the oxidation potential for U(IV)/U(VI) is considerably lower than for Fe(II)/Fe(III) couple (see the supplementary figure S2). The corresponding values of the isomer shift and the hyperfine field (table S1) indicated the magnetic field due to haematite and iron hydroxides (see supplementary information).

4.8 Remediation

Uranium being radiologically and chemically toxic is a big environmental hazard and earlier studies have revealed that people living in phosphatic mining zone had higher concentration of uranium in their blood rather than the people staying in urban dwelling (Menzel 1968; Philip *et al.* 1979; Cevik *et al.* 2010; Albedri *et al.* 2014; Sahu *et al.* 2014).

With respect to the above characterisation data, the strategies for remediation should be devised based on the presence of uranium as a substituent in the structure and also on its adsorption on silica and other clay minerals. Due to the entrapment of the uranium in the structure of haematite and FAP, leaching with mild complexing agents such as sodium bicarbonate solutions and citric acid will not serve the purpose. Encapsulation of the soil with cement and lime will also be less effective in remediating the uranium from the structure. Besides, these would cause a negative effect on the structure and composition of the soils. However,

these remediation studies will work in the case of uranium being adsorbed on silica and other clay minerals. Since no prominent hexavalent uranium species has been noted this implies that magnetic separation will not work.

A cost-effective strategy for the remediation of these lands would be phytoremediation and bioremediation. Since the Bijawar region is devoid of any organic species and plant nutrients hence phytoremediation will not serve the purpose. In bioremediation, the U(VI) reducing microorganism such as *Desulfovibrio desulfuricans*, *Pseudomonas aeruginosa* and *Rhizopus arrhizus* are effective in leaching out uranium from low- and intermediate-grade uranium reserves. These bacteria reduce U(VI) to U(IV) and also solubilise elements as a result of acid production. The microbial communities that are effective in this process are Geobacteraceae. Besides, the bioremediation is an environment-friendly process unlike leaching with other chemical agents. The process is highly effective in cases where other remediation techniques will not work.

5. Conclusion

To summarise, extensive mineralogical and spectroscopic characterisations have been carried out on the uraniferous mineral concentrate portion obtained from the phosphatic rocks of the Bijawar region for speciation of uranium in this region. The structural characterisation identified FAP and haematite to be the main phases in the mineral concentrate portions along with traces of calcite. The powder X-ray diffractometry confirmed the hexagonal structure of the FAP material with lattice parameters $a = 9.397 \text{ \AA}$ and $c = 6.884 \text{ \AA}$.

Haematite is also identified to be of hexagonal structure with lattice parameters $a = 5.032 \text{ \AA}$, $b = 5.032 \text{ \AA}$, $c = 13.76 \text{ \AA}$. Functional groups of two phases have been confirmed by FTIR and Raman spectroscopy. Molecular spectroscopic studies have indicated both the hexavalent and tetravalent oxidation states for uranium in these mineral concentrate samples. The PL data from the subsurface sample has indicated that in the tetravalent state, U^{4+} is identified to be substituted at the Ca(II) sites in the FAP. In the hexavalent U(VI) state, it is identified in the form of uranate ion $(\text{UO}_6)^{6-}$ potentially as a substituent of the Ca^{2+} ion in FAP and that of Fe^{3+} ion in haematite and finally as $(\text{UO}_2)^{2+}$ adsorbed on silica. The fluorescence decay lifetime studies carried out by TRPL of the $5f\ 6d-5f^2$ transition for U^{4+} : FAP was measured to be 2–4 ns. In the hexavalent U(VI) state, fluorescence lifetime decay was calculated to be of the order of $10\ \mu\text{s}$. Lifetime studies carried out by TRPL and the oxidation state analysis by XANES further corroborated the PL findings. This study aims to provide a spectral database of uranium species in the Bijawar region. Based on the above characterisation data, bioremediation is identified to be an effective strategy for remediation in this area.

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