Structural and Luminescent Characterization of Uraniferous Fluorapatite and Haematite associated with Phosphatic Rocks of the Bijawar Group in Sagar Distt., Madhya Pradesh (India).

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Supporting Information

Abstract:

The structural and spectroscopic characteristics of phosphatic ferruginous shale samples from Bijawar Group rocks from Sagar District of Madhya Pradesh (India) have been probed for identification of uranium species. Fluorapatite (Ca$_5$(PO$_4$_3)F), (FAP) and haematite ($\alpha$-Fe$_2$O$_3$) were identified as the main phases in the separated mineral concentrates. The photoluminescence (PL) and near edge spectroscopy X-ray absorption (XANES) studies pointed to strong experimental evidence of both U(IV) and U(VI) oxidation state 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 that has been attributed to the substitution of Ca$^{++}$ ions by U(IV) in FAP and broad structureless emission due to stabilization of U(VI) as UO$_6$$^{6-}$ in haematite. Time-resolved spectroscopy studies have revealed bi-exponential decay components lasting 2-5 ns for
U(IV) species and 10μs for U(VI) species. These characterizations revealed fundamental information about the oxidation state and form of uranium in this region. Remediation measures for Bijawar region are also suggested.

Keywords: Uranium, Photoluminescence, X - ray absorption spectroscopy, X-ray diffraction

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1. INTRODUCTION

The need for nuclear self-sufficiency and the growing gap between energy demand and supply has necessitated country to utilize modest (low and intermediate) indigenous uranium reserves. Phosphate deposits are large potential sources of low grade (0.005-0.020%) uranium reserves worldwide. In India, the total reserve of rock phosphates is about 296.3 million tones, which could serve as significant secondary source of uranium. 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 substantial quantity of low grade uranium. (Banerjee et al. 1982; Roy et al. 2004; Dar et al. 2014a). Uranium mineralization in Bijawar basin is hosted by phosphatic ferrounginous shale breccia and the average concentration of uranium varies approximately between 150 ppm to 0.1%.

Previous structural and spectroscopic characterization studies conducted in the Bijawar region and Paleoproterozoic 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; Dar et al. 2014b) have focussed 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 characterization of uranium species in 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 characterization and speciation of uranium in Bijawar region.

An important key to understand uranium retention process (adsorption, precipitation or association with minerals) is to identify the uranium species. The mobilization 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 uranium speciation. Hence the techniques that can be used as diagnostic tool at the molecular level such as luminescence spectroscopy, X-ray absorption spectroscopy Raman spectroscopy are employed.

In the present investigations, a comprehensive PL study along with lifetime decay by time resolved photoluminescence (TRPL) has been carried out on the sample from 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 characterization performed using XANES, XRD, Raman spectroscopy, Fourier Transform Infrared (FT-IR) spectra and SEM. 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 has been utilised to infer the state of uranium in investigated mineral phase eg. FAP and hematite. Also the data has been utilised to evaluate the remediation aspects for this region.

2. GEOLOGY

Bijawar region is located in the Chattarpur district of Madhya Pradesh, India (Fig.1). The Paleoproterozoic metasedimentary rocks of Bijawar Group resting upon the Archean Bundelkhand Basement Complex are overlain by the rocks of Vindhyan Supergroup (Jha et al. 2012). The study area constituted Proterozoic Bijawar basin exposed 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 mineralization in this area is hosted by ferruginous shale breccia with angular and sub rounded fragments of quartz in 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 characterization was collected from Bijawar region during field season 2014-2015 during reconnaissance survey (geological coordinates 24° 20′ 52.5′′ N, 79° 12′ 51′′ E). SH-9 sample is a typical combination of FAP, iron oxides, hydroxides and oxyhydroxides along with cementitious silica, quartz and clay mineral. Optical microscopy and solid state nuclear track detector (SSNTD) studies conducted on the sample have indicated Fe rich material (hematite) and FAP as the main uranium bearing radioactive phases. (Fig. S1), (see supporting information). The sample has clear partitioning available in form of black and white portion constituting of FAP and haematite. SH-9 was hence separated into FAP bearing white portion called SH-9White (SH-9W) and hematite bearing black portion hereby called SH-9Black (SH-9B). The representative subsamples of 100 gm quantity from each of the lots, SH-9W and SH-9B were powdered (mesh size -60) and homogenized by coning and quartering. 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”× 4” with a multichannel analyzer. The % U₃O₈ content in SH-9W and SH-9B are identified to be 0.17 % and 0.053% respectively. In order to beneficiate the corresponding minerals, the samples were crushed to size (0.15 mm<grain size< 0.17 mm) and subjected to heavy liquid separation. The crushed samples were first subjected to bromoform separation (specific gravity, ρ=2.89 g/cm³) to selectively concentrate the mineral species. The bromolight portion of the samples consisting of quartz, mica and clay minerals were discarded and bromoheavy portion containing uranium species for both mineral concentrate was further subjected to methylene iodide (ρ=3.35 g/cm³) separation. This mineral concentrate portion of both SH-9W and SH-9B was selected for analysis. Phase purity and crystal structure of the mineral concentrate samples were identified by X ray diffractometer using Cu Kα radiation (1.5406 Å) 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 measured XRD data was carried out using refinement software. Surface morphology along with qualitative and semi quantitative analysis of the fractured mineral was analyzed with field emission scanning electron microscope (FE-SEM) (Carl-Zeiss, SUPRA 40) equipped with X-ray energy dispersive spectroscopy (EDS). Raman spectra were obtained using a Raman spectrometer with an excitation source of 785 nm with spectral resolution of 1 cm\(^{-1}\) (Reinshaw Invia). Infrared absorption spectra were taken in the range from 400 to 4000 cm\(^{-1}\) using FTIR using standard KBr technique (Perkin-Elmer). The optical absorption was measured in the spectral range from 190-700 nm using UV-vis-NIR spectrometer (UV 3101 PC Shimadzu). The photoluminescence (PL& PLE) spectra were measured using a FLS920 fluorescence spectrometer (Edinburgh Instruments Ltd). For excitation, a 450W 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 5MHz) and a xenon microsecond (\(\mu\)s) flash lamp using FLS920 lifetime spectrometer (Edinburgh Instruments Ltd.). XANES spectra of the samples were recorded in fluorescence mode at U L\(\text{III}\) edge (17116 eV) and those of standards were taken in transmission mode using vortex energy detector at BL-9, Scanning X-ray absorption fluorescence spectroscopy (EXAFS) Beamline of INDUS-2 Synchrotron Source (2.5 GeV, 100mA) at Raja Ramanna Center for Advanced Technology (RRCAT), Indore.

4. RESULTS AND DISCUSSION

The structural and spectroscopic characterization pertaining to SH-9W(FAP) and SH-9B (hematite) are discussed below:

4.1 X-ray Diffraction

Fluorapatite: Qualitative analysis of the XRD revealed FAP to be the main phase of SH-9W. (Fig. 2(a)). The intense \(2\theta\) reflections at 25.89°, 29.01°, 31.90°, 32.20°, 33.10°, 34.16°, 39.94°, 46.87°, 49.57° and 51.41° *2\(\theta\) corresponding to the \(hkl\) planes (002), (120), (121), (112), (300), (202), (310), (222), (123) and (410) 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 hematite [JCPDS #33-0664]. The structure of FAP is hexagonal belonging to the space group P6₃/m with unit cell dimensions of a = b = 9.367 Å, c = 6.884 Å and cell volume 519.77 Å³. The crystal refinement of the recorded X-ray diffraction 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 Å, c = 6.878 Å, α = 90°, β = 90°, γ = 120°, lattice volume, V = 525.96 Å³ and space group P6₃/m. Relatively weak agreement was observed between the experimental and simulated structure (weighted residual error, Rwp = 24%) due to the presence of impurity phases. The different crystallographic sites of FAP can accommodate a variety of rare earth elements and radionuclides, therefore one possible explanation may be due to the occupancy of the Ca(I) and Ca(II) sites by rare earth dopants (Hughson and Sengupta 1964; Kay et al. 1964; Mackie et al. 1972; Gunawardance et al. 1982; Cockbain et al. 1967; Nary Szabo. 1930)

The structure of FAP has been well reported in literature (White and Zhili 2003, Nary Szabo. 1930, Beeveres C.A. 1946). 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 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 C₃, with each Ca having six oxygen nearest neighbours that form a distorted triangular prism about the Ca²⁺ ion. The Ca(II) site has Cs 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 P6₃/m has been shown in the inset of Fig. 2(a). No distinct peaks corresponding to any uranium mineral was obtained indicating that uranium has been substituted at the lattice site rather than at the interstitial site.

**Haematite:** The XRD pattern of SH-9B (Fig. 2(b)) 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 indicating haematite to be the main phase [JCPDS # 33-0664]. The crystallographic parameters identified are structure: hexagonal, space group: R3C, lattice parameter a = 5.032 Å, b = 5.032 Å, c = 13.76 Å, α = 90°, β = 90°, γ = 120° and V = 301.78 Å³ which are close to the values reported in the literature of pure hematite phase a= b= 5.038 Å, c=13.77 Å, V= 302.72 Å³ (Pauling L and Henrick S.B. 1925, Willis et al. 1952). A small
(Rwp=13%) values of the structure refinement in 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.

**Fluorapatite:** Raman spectra of samples SH-9W is shown in Fig. 2(c). The modes corresponding to the stretching, translational and internal vibration modes of the PO$_4$ groups are visible in the spectra. A strong band is observed at 964 cm$^{-1}$ characteristic of the $v_1$ asymmetric stretching of the PO$_4$ group while the bands at 1058 and 1083 corresponds to PO$_4$ $v_3$ anti-symmetric stretching band and those at 403 and 439 to $v_2$ anti-symmetric stretching band (Comodi et al. 2001). However no bands corresponding to the uranium species were visible.

**Haematite:** In case of SH-9 B (Fig. 2(d)) 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 2001). The Raman spectral peak of haematite corresponds to a well crystallized structure. The bands corresponding to 657 cm$^{-1}$ indicated the presence of small amount of lepidocrocite (γ-FeOOH). Haematite is a mineral formed by weathering process in the soils, hence there is high possibility of it being present along with iron oxides like lepidocrocite (γ-FeOOH) or goethite (α-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.

**Fluorapatite:** The FTIR spectra of SH-9W mainly demonstrated the vibrational modes for PO$_4^{3-}$ and CO$_3^{2-}$ in the FAP (Fig. 2(e)). Peaks at 470, 573, 601, 964, 1056, 1093 cm$^{-1}$ are characteristic
bands of PO$_4$ group (Stoch et al. 1999). 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 $\nu_3$ vibration mode, which was visible at 1056 and 1093 cm$^{-1}$. The bands at 572 and 601 cm$^{-1}$ are the $\nu_4$ vibration mode of the phosphate group. In addition, a doublet appears at 1429 and 1490 cm$^{-1}$ corresponding to the $\nu_3$ vibration mode and the band centred at 869 cm$^{-1}$ for $\nu_2$ vibration mode of the carbonated groups. The peaks at 1999 and 2088 may be due to PO$_4^{3-}$ overtones (Azami et al. 2011).

**Haematite:** Fig. 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 (Betanchur et al. 2012). The other bands at 946 and 1056 cm$^{-1}$ are due to symmetric stretching bands of PO$_4$ group due to the impurity phase of FAP in it. The presence of bands at 1632 cm$^{-1}$ indicates $\nu_2$ bending modes of water, which proves structurally in equivalent water molecules in the crystal structure.

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

4.4 Surface Morphology studies

**Fluorapatite:** Fig. 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 homogenous or heterogeneous crystallizations. Semiquantitative analysis using EDX revealed the Ca/P ratio of 1.76 in FAP.

**Hematite:** Fig. 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 well crystallized structure.

Fig. 3(c) and Fig. 3(d) indicate 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 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 Photoluminescence studies (PL)

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

The difference in the spectral luminescence of U(IV) and U(VI) species helps in their detection and discrimination in complex rock matrix. PL studies were therefore conducted to identify different uranium species. The absorption spectrum of SH-9 sample is indicated in Fig. 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 from 250-700 nm. The absorption spectra exhibited a relatively broad and smeared out transition in the 33000-45000 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 5f² (ground state of uranium) and 5f 6d states, namely f-d transitions that occur in energy above 27000 cm⁻¹. The intense absorption spectra corresponding to the lowest energy level is observed at 230 nm (43478 cm⁻¹), which is 15000 cm⁻¹ lower than that of free U(V), (U⁴⁺) ion since the lowest f-d transition corresponding to U(V) is placed at 59183 cm⁻¹. The optical band gap of the sample was determined to be 4.5 eV.

Fluorapatite: Fig. 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 excitation wavelength. The deconvolution of the emission spectra revealed sharp peaks at 290 nm, 313 nm, 348 nm and 399 nm.

The spectral effects could be explained by the 5f-6d orbital hybridization of uranium under the influence of crystal field. Several other studies have also reported similar luminescence of U(IV) and U(III) covalent compounds in different crystal field symmetry and matrices; U⁴⁺ in
Cs₂UCl₆ (O₆ symmetry) (Satten et al. 1965), U⁴⁺ in UCl₄ and ThCl₄ (D₂d symmetry) (Malek et al. 1984), [Li(THF)₄][UCL₅(THF)] (C₄ᵥ symmetry) (Hashem et al. 2013), U⁴⁺ in UF₄ (Carnall et al.), U⁴⁺ doped LiYF₄ single crystal (Godbole et al. 2001), U⁴⁺ doped into YF₃ single crystal (Kirm et al. 2003) and sulphate complexes in a frozen matrix (Gorller 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 was observed by Panckzer et al. 1998.

Uranium has a ground state electronic configuration of 5f³6d¹7s². Uranium (V) has two unpaired electrons in the 5f state and electronic ground state of uranium is 3H₄. These emission spectra might be assigned to either excitation into a band of f-d and LMCT (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 5f² configuration or due to the f-f transitions from ¹S₀ to lower 5f levels of uranium (Hashem et al. 2013). Both these intra configurational f-f transitions and inter configurational 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 (Fig. 4(b)) and the excitation wavelength is observed at 230 nm which corresponds to 5f² - 5f6d transition. (Kirishima et al. 2004). The interconfigurational 5f6d-5f transitions are parity-allowed unlike 5f-5f transitions which are parity forbidden. They are characterized by short emission lifetimes and emission bands of high intensity located in the UV range. Radiative transitions from 5f6d to 3H₅, 3F₃, 3H₆ and 3P₀ resulted in emission peaks at ca. 290 nm, 313 nm, 348 nm and 399 nm. The positions of the energetic bands are dependent on the coordination environment, crystal field symmetry and excitation wavelength of the material. Fig. 6 shows the band energy diagram of U⁴⁺ 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 (Sr²⁺, Pb²⁺, Ba²⁺, Mn²⁺ and Cd²⁺), trivalent rare earth element (REE³⁺) and tetravalent actinide (Th⁴⁺ and U⁴⁺) cations (Lu et al. 2009). The Ca site occupancy of rare earths 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 are described as having coordinated to nine oxygen atoms with point group symmetry C₃ whereas
the Ca(II) sites in the 6h Wyckoff positions (effective radius 1.06 Å) are eight coordinated to seven O atoms and one F atom having Cs symmetry (Elliot et al. 2002). According to Shannon et al. 2002, the U(IV) in FAP having nine folds coordination (effective radius 1.05 Å) substitutes at the Ca(II) position. The charge imbalance created by the substitution of higher valent U⁴⁺ is compensated by the coupled substitution involving Na⁺, Si⁴⁺ and vacancies (Elliot, 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 (Fig. 3(c) and Fig. 3(d)). So the local charge compensation may be maintained by the following coupled substitution in SH-9W.

\[ \text{M}^{4+} + [\text{vacancy}] = 2\text{Ca}^{2+} \]
\[ \text{M}^{4+} + 2\text{Na}^+ = 3\text{Ca}^{2+} \]
\[ \text{M}^{4+} + 4\text{Na}^+ = 5\text{Ca}^{2+} \]

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

The spectra of SH-9W under 285nm excitation with xenon lamp and filter at 335 nm can be deconvoluted into two structured emissions in the range from 300 nm- 450 nm and 450 nm - 500 nm (Fig. 5(b)). The transitions at 313 nm (5f⁴6d¹-3F₃), 319 nm (5f⁴6d¹-3F₄), 348 nm(5f⁴6d¹-3H₆), 409 nm (5f⁴6d¹-1D₂) and 448nm (5f⁴6d¹-3P₁) are attributed to the signature of U⁴⁺ as discussed above and an inhomogeneously broadened and smeared out emission spectrum without any band resolution in the spectral range from 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 hexavalent state uranium, can exist as (UO₂)²⁺ or U(VI) in tetrahedral coordination; (UO₄)²⁻ or uranium in octahedral coordination; (UO₆)⁶⁻. While (UO₄)²⁻ emits in the orange red region, both UO₂²⁺ and octahedral UO₆⁶⁻ emit in the green region. Both these uranyl and uranate emissions are electric dipole parity forbidden transitions however UO₂²⁺ emission can be distinguished from that of the latter on the basis of its characteristic vibronic structure exhibiting set of equidistant lines. The absence of vibronic structure clearly indicated that the transition intensity is from electronic origin due to substantial electric dipole change during 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: SrZO₃, U: SrB₄O₇ (Tanner et al. 1997). The origin of this emission is assigned to the parity forbidden charge transfer transition 5f–t₁ᵤ 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 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 case of U$^{6+}$ substitution in FAP takes place according to the formula:

$$M^{6+} + 2Si^{4+} = Ca^{2+} + 2P^{5+}$$

$$M^{6+} + 2Si^{4+} = Ca^{2+} + 4P^{5+}$$

On excitation with 350 nm, laser two spectral components arise from three chemically different species in SH-9W (Fig. 5(c)). 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 case of 245 nm. The second component signified intense emission of red colour in the range from 550-700 nm. These strong emissions at 578 nm, 620 nm and 660 nm could be attributed to rare earth ions. The photoluminescence 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 (Fleet et al. 1995) have noted that the structural role of rare earth elements REE in apatite remains unknown, as a given REE may be distributed over both 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 Laporte selection rule. However the transitions become permissible for Eu$^{3+}$ occupancy at the Cs non centrosymmetric site. The luminescence of Eu substituted apatite has been widely studied by (Gaft et al.2001; Blasse et al. 1975) 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 ICP-AES analysis revealed the corresponding values (La: 8ppm; 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 transition of Dy$^{3+}$ between $^4F_{9/2}$ and $^6H_{13/2}$ transition 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.
Though XANES measurements have indicated U(IV) state for SH-9W, PL have indicated both U(IV) and U(VI) state for both of the samples which is due to the higher sensitivity of PL when compared to XANES.

Fig. 4(b) showed the excitation spectra of SH-9W corresponding to the emission bands at 313nm, 336 nm, 400 nm corresponds to the same broad band extending from 190 nm to 250 nm. The excitation spectra due to the emission at 470 nm, Fig. 4(c) also revealed the similar feature. Hence the excitation spectra can be explained due to the spectral overlap of charge transfer transition from $5f^2 \rightarrow 5f6d$ charge transfer transition and oxygen (2p) to uranium (6d) orbitals.

**Hematite:** Fig. 5(d) shows the PL emission spectrum of SH-9B in the range from 250 nm to 450 nm at an excitation of 245 nm. The feeble emission peaks in the near UV region is 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 structure less emission at 470 nm (Fig. 5(e)). 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 (Dodge et al. 2002; Dzombak et al. 1990; Finch et al. 1999; Hsi et al. 1985; Waite et al. 1994), 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 co-precipitation with iron oxides with incorporation of a uranate species ($U^{6+}$) in the haematite structure (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/de-protonation 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 nm and 669 nm on excitation with 350 nm in SH-9B (Fig. 5(f)) of transitions is due to the presence of Eu ions present in FAP at lower symmetry site Cs. The excitation spectra of SH-9 while keeping the detector at 590 nm revealed the characteristic f-f transition corresponding to the $^7F_0 \rightarrow ^5L_6$ transition of Eu$^{3+}$ ions. (Fig. 4(d)). PL emission indicated the presence of U(IV) and U(VI) species apart from rare earth ions.
4.6 Time Resolved Photoluminescence (TRPL)

**Fluorapatite:** The TRPL decay curves of SH-9W at 313 nm, 336 nm and that of SH-9B at 470 nm are shown in Fig. 7(a), Fig. 7(b) and Fig. 7(c) respectively. We note that the lifetimes are bi-exponential 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 bi-exponential function using the equation where $A_1$ and $A_2$ are pre-exponential factors and $\tau_1$ and $\tau_2$ stands for the lifetime of fast and slow decays. The observed effective lifetime $\tau$ for bi-exponential 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 biexponential decay indicating the presence of two distinct U(IV) species. This biexponential decay could have arisen due to the stabilization of U(IV) in two coordination environments; either Ca(I) in sevenfold coordination or Ca(II) in nine fold coordination.

**Hematite:** The decay measurements of SH-9B at 470 nm, Fig. 7(c) revealed two different decay times in the range of $\mu$s, characteristic of uranate ion. Lifetime values obtained are 10.49 $\mu$s (69%) and 1.12 $\mu$s (31%). The uranium in uranyl form has lifetime in the range of 100’s of $\mu$s however in the present case the lifetime has clearly indicated that the uranium is present as uranate ion.

4.7 $UL_{III}$ edge XANES analysis

X-ray absorption spectroscopy (XAS), containing X-Ray absorption near edge structure (XANES) has become a well established tool for oxidation state determination of actinides. XANES have been carried out on SH-9W and SH-9B Uranium $L_{III}$ edge absorption in fluorescence mode. The calibration for energy was performed by measuring the edges of the natural reference samples; Rutherfordine (UO$_2$CO$_3$) for U(VI)) and uraninite (UO$_2$) for U(IV), the inflection points of which were obtained at 17165.3 eV and 17167.9 eV respectively.
Fluorapatite: In case of the spectra for SH-9W, U L₃-edge edge jump position (eV) is obtained at 17163.9 eV indicating that uranium in FAP rich portion is present in tetravalent state; U(IV) state which implies that either U⁴⁺ has substituted Ca²⁺ ions. (Fig. 8(a)).

Hematite: The U L₃-edge jump position (eV) for SH-9 B has been obtained at 17167.9 eV which is similar as UO₂CO₃ standard, revealing that SH-9 B has U(VI) oxidation state (Fig. 8(b)). 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 dixoo linear moiety (a UO₂²⁺ ion group). Most U(VI) solids and solution species have a coordination number (CN) of six to eight (Burns et al. 1996; Weigel et al. 1986; Duff et al. 2000) whereas U(IV) in UO₂(s) for example, usually has a CN of eight or nine, and does not have a “shoulder”. Since XANES spectra of SH-9 B has very similar shoulder at post-edge side as UO₂CO₃ XANES standard of U(VI) which indicated that uranium has possible local coordination of octahedral or close to it. However the studies have suggested that U(VI) in the form of UO₆⁶⁻ replaces the Fe³⁺ ion.

The Mossabeur 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 hexavalent form since the oxidation potential for U(IV)/U(VI) is considerably lower than for Fe(II)/Fe(III) couple (see supporting information S2).

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 (Sahu et al. 2014; Menzel et al. 1968; Albedri et al. 2014; Cevik et al. 2010).

With respect to the above characterization 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 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.

An effective 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 microporganism 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 element as a result of acid production. The microbial communities that are effective in this process are Geobacteraceae. Besides 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 characterization have been carried out on the uraniferous mineral concentrate portion obtained from the phosphatic rocks of Bijawar region for speciation of uranium in this region. Structural characterization identified FAP and haematite to be the main phases in the mineral concentrate portions along with traces of calcite. Powder X ray diffractometry confirmed the hexagonal structure of the FAP material with lattice parameters \( a = 9.628 \, \text{Å} \) and \( c = 6.764 \, \text{Å} \). Haematite is also identified to be of hexagonal structure with lattice parameters \( a = 5.032 \, \text{Å}, \ b = 5.032 \, \text{Å}, \ c = 13.76 \, \text{Å} \). Functional groups of two phases have been confirmed by Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy. Molecular spectroscopic studies have indicated both hexavalent and tetravalent oxidation state for uranium in these mineral concentrate samples. PL data from the subsurface sample has indicated that in tetravalent state, \( \text{U}^{4+} \) 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 \( \text{(UO}_6\text{)}^{6-} \) potentially as a substituent of the Ca\(^{2+}\) ion in FAP and that of Fe\(^{3+}\) ion in haematite and finally as \( \text{(UO}_2\text{)}^{2+} \) adsorbed on silica. The fluorescence decay lifetime studies carried by TRPL of the 5f
6d-5f² transition for U⁴⁺: FAP was measured to be 2-4 ns. In the hexavalent U(VI) state, fluorescence life time decay was calculated to be of the order of 10 µs. Life time studies carried by TRPL and oxidation state analysis by XANES further corroborated the photoluminescence findings. This study aims to provide a spectral database of uranium species in Bijawar region. Based on the above characterization data, bioremediation is identified to be effective strategy for remediation in this area.

ASSOCIATED CONTENT

Supporting Information

Optical microscope and SSNTD studies

Petromineralogical studies of selected samples were carried out using transmitted and reflected light microscopy. Chromogram (using HNO₃, Potassium ferrocyanide and NaOH) studies for presence of leachable U mineral and auto radiography using alpha ray sensitive CN-85 for locating radioactive minerals were adopted prior to petrological study. The corresponding optical micrographs are shown in Fig S1.

Mossabeur spectroscopy

Mossabeur measurements were carried out using ^{57}Fe and ^{119}Sn in the transmission modes. Mossabeur spectroscopy provides information about the local environment of iron ions due to the presence of convenient active isotope of ^{57}Fe. Fig. S2 representing the room temperature mossabeur spectra of SH-9 sample which can be considered as the superposition of two sextets with different hyperfine fields and similar isomer shifts but essentially zero quadrouple splitting. The outer sextet gives a hyperfine value of BₜPointSize=51.8T corresponding to a well crystallized haematite (BₜPointSize= 51.8 T) (Murad et al. 1986) implying that haematite is the major phase in the sample, where as the inner sextet gives the value of (BₜPointSize= 38.9T). This hyperfine magnetic field arises due to either iron hydroxides or magnetites. The magnetic particles smaller than 15-20 nm
gives rise to paramagnetic doublet indicating a broad size distribution of magnetic particles. This may be assigned to a superparamagnetic haematite (Fe₂O₃) along with some amount of lepidocrocite (γ-FeOOH). Presence of Fe³⁺ in the samples indicate a predominantly oxidising atmosphere where most of the uranium would have oxidized to U(VI) state (Dodge et al. 2002). Corresponding values of the isomer shift and hyperfine fields are given in Table: 1. These results indicate the presence of uranium in U(VI) form in this region (The results of study on other samples would be further communicated).

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**Figure Caption**

Fig 1. Geological map of investigated area of Bijawar basin.

Fig. 2 Structural characterization of SH-9W and SH-9B showing vibrational and structural information. The measured XRD patterns of (a) SH-9W showing predominantly FAP bands (The inset shows the schematic representation of hexagonal structure of Fluorapatite 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 corundum structure of Fe$_2$O$_3$. The face sharing and edge sharing FeO$_6$ octahedra are shown stucked 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 and (e) FTIR pattern of SH-9W and (f) SH-9B respectively.

Fig. 3 SEM micrograph of (a) Magnified view of SH-9W (b) SH-9B (c) The SEM micrograph, in BSE mode, of the whole rock sample of SH-9,(The inset shows 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 inset shows the EDX spectrum revealing the presence of actinides, U and Th).

Fig. 4. (a) UV-vis-NIR spectra of SH-9 showing 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) (d) PL excitation of SH-9 while keeping the detector at 590 nm showing the characteristic excitation peak of Eu.

Fig. 5. Photoluminescence emission spectrum of (a) SH-9W ($\lambda_{exc}=245$ nm) showing 5f6d-5f$^2$ transitions (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$$^{5-}$ ion. (c) SH-9W ($\lambda_{exc}=350$ nm) The right inset indicates transitions at 620 nm, 669 nm and 578 nm due to Eu$^{3+}$ and Dy$^{3+}$ ions. (d) SH-9B ($\lambda_{exc}=245$ nm) (e) SH-9B ($\lambda_{exc}=285$ nm) (f) SH-9B ($\lambda_{exc}=350$ nm) excitation.

Fig. 6. Band energy diagram of U$^{4+}$ ion.

Fig. 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).

Fig. 8 (a) U L$_3$-edge XANES spectra of 4+, 6+ and SH-9W, SH-9B samples b) 1$^{st}$ derivative of XANES spectra.
Fig. S1 Alpha tracks (α) corresponding to ferruginous encrustation of phosphatic ferruginous shale.

Transstructural (b) Photomicrograph of phosphatic ferruginous shale showing dark coloured phosphatic groundmass. Trans. 1N. air.

Fig. S2 Mossabeur Spectra of SH-9 whole rock sample.

Table :1 Average magnetic hyperfine field ($B_{hf}$), isomer shift and quadrouple splitting of SH-9
<table>
<thead>
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<th>Sample</th>
<th>IS</th>
<th>QS</th>
<th>BHF</th>
<th>Area</th>
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<tr>
<td>I sextet</td>
<td>$0.38 \pm 0.01$</td>
<td>$-0.18 \pm 0.1$</td>
<td>$51.04 \pm 0.06$</td>
<td>44</td>
</tr>
<tr>
<td>II sextet</td>
<td>$0.38 \pm 0.01$</td>
<td>$0.25 \pm 0.01$</td>
<td>$35.95 \pm 0.08$</td>
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<tr>
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<td>$1.24 \pm 0.04$</td>
<td>WID 0.45</td>
<td>9</td>
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