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Geochemical and U-Th isotopic insights on uranium enrichment in reservoir sediments HPSTAR 1188-2021

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ABSTRACT

Uranium (U) geochemistry and its isotopic compositions of reservoir sediments in U mine area were poorly understood. Herein, U and Th isotopic compositions were employed to investigate source apportionment and geochemical behavior of U in 41 reservoir sediments from a U mining area, Guangdong, China. The remarkably high contents of both total U (207.3–1117.7 mg/kg) and acid-leachable U (90.3–638.5 mg/kg) in the sediments exhibit a severe U contamination and mobilization-release risk. The U/Th activity ratios (ARs) indicate that all sediments have been contaminated apparently by U as a result of discharge of U containing wastewater, especially uranium mill tailings (UMT) leachate, while the variations of U/Th ARs are dominated by U geochemical behaviors (mainly redox process and adsorption). The U isotopic compositions (δ^{238} U) showed a large variance through the sediment profile, varying from -0.62 to -0.04%. The relation between δ^{238} U and acid-leachable U fraction demonstrates that the U isotopic cativity) and subsequent biogeochemical processes. The findings suggest that U-Th isotopes are a powerful tool to better understand U geochemical processes and enrichment mechanism in sediments that were affected by combined sources and driving forces.

1. Introduction

With increasing global demands for energy, radioactive uranium (U) industry has been growing rapidly and led to severe environmental contamination (Basu et al., 2015; Cumberland et al., 2016; Dang et al., 2018a; Kipp et al., 2009; Yin et al., 2019, 2020, 2021). In these processes of U industry, numerous amounts of by-product wastes and uranium mill tailings (UMT) containing radioactive elements (e.g., U, Th and Ra) and other toxic elements (e.g., Pb, Zn and Cu) have been discharged into the

environments (Basu et al., 2015; Cumberland et al., 2016; Dang et al., 2018a; Wang et al., 2016, 2017). U-bearing wastes typical of UMT were often disposed in an open-air, entailing high risks of U contamination in ambient surface/ground waters and aquatic systems (Yin et al., 2019). Thus, to better understand the occurrence, behavior and fate of U in mining areas, especially the rarely concerned reservoir environments, has become one of the essential issues in U environmental geochemistry and associated remediation strategy (Cumberland et al., 2016; Dang et al., 2018a; Wang et al., 2019).

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As a redox-sensitive element, U mostly occurs in U(IV) and/or U(VI) in natural environments. The mobility of U strongly depends on the redox state. Under reducing environments, U predominantly presents as U(IV) which is relatively insoluble, while highly soluble U(VI) mostly exists in the oxidizing environment (Scott et al., 2005; Selvakumar et al., 2018). The ability of U(VI) adsorption on sediments is strong at pH 6–7, and significantly reduced at pH 8, largely depending on the aqueous pH (Crawford et al., 2017). Dissolved U is mainly consisted of free uranyl ions (UO_2^{2+}) and various complexes (Wang et al., 2019). UO_2^{2+} can complex with ligands (e.g., phosphate, sulphate, silicate, carbonate, vanadate and hydroxyl), either increasing (via forming stable aqueous complexes) or decreasing (via forming insoluble minerals) U mobility in aquatic system (Latta et al., 2016; Crawford et al., 2017; Gilleaudeau et al., 2019). Dissolved organic matter (OM) can facilitate its transportation of U, and prevent its adsorption to mineral surfaces (Cumberland et al., 2018; Tinnacher et al., 2013; Zhao et al., 2012), while colloidal/particulate OM would promote the formation of OM-rich sedimentary U deposits (Cumberland et al., 2016, 2018; Greenwood et al., 2013). Fuller et al. (2020) revealed that U(VI) can complex with carboxylate groups of the OM. Moreover, U(IV) can adsorb to OM and OM-coated clays, suggesting that U(IV) would be more mobile under reducing conditions and more sensitive to redox fluctuations than anticipated (Bone et al., 2017).

In nature, U occurs as ²³⁸U, ²³⁵U and ²³⁴U, with proportion of 99.284%, 0.711% and 0.0058%, respectively. Due to the long half-life of 238 U (~ 4.47 × 10⁹ years) and 235 U (0.704 × 10⁹ years), U mass fractionation caused by natural radioactive decay is negligible. ²³⁸U and ²³⁵U are deemed as stable isotopes. U isotopes have been applied successfully as a potential tool for investigating U redox processes, transport and origin in the environment (Dang et al., 2018a,b; Lau et al., 2020; Murphy et al., 2014; Weyer et al., 2008). The significant U isotopic fractionation between mineralised sediments and groundwaters indicated that the reduction of U(VI) to U(IV) and precipitation of U minerals preferentially incorporated ²³⁸U into sediments (Murphy et al., 2014). Modern coastal sediments showed a large δ^{238} U (U isotopic composition, viz. 238 U/ 235 U atomic ratio relative to that of U isotopic standard) variation, meanwhile sediments lied in front of river mouths had higher $\delta^{238} U$ values than other coastal sediments, and suggested that promoted diffusion in coarser sediments relative to fine sediment may generate more effective isotope fractionation (Dang et al., 2018a). δ^{238} U values in sediments and waters from Bow Lake located adjacent to a former U mine had estimated the U from mixing of two sources, which were further confirmed by Pb isotopes and other biogeochemical approaches (Dang et al., 2018b). Uranium isotopes have also been applied to evaluate U removal in remediation operations (Bopp et al., 2010; Stylo et al., 2015).

The remarkable discrepancy of solubility for U/Th can lead to the fractionation of 230 Th, 232 Th, 234 U, and 238 U (Dawood, 2010; Kipp et al., 2009; Robinson et al., 2008; Yusoff et al., 2015). Thus, in addition to U isotopes, U/Th activity ratios (ARs) (e.g., 234 U/ 238 U, 232 Th/ 238 U and 230 Th/ 232 Th) can also be used to investigate the origin of U/Th and unveil U/Th enrichment mechanisms in environment (Robinson et al. 2008; Kipp et al., 2009; Dawood, 2010; Yusoff, et al., 2015). Studies have exhibited that 234 U/ 238 U, 232 Th/ 238 U and 230 Th/ 232 Th ARs were employed to evaluate the detrital, authigenic and anthropogenic input of U/Th to sediments (Dawood, 2010; Kipp et al., 2009; Robinson et al., 2008; Yusoff et al., 2015).

However, hitherto very limited studies have revealed U geochemical behaviors and its isotopic composition in sediments, where affected by long-term U mining and metallurgical activities. Further investigation is required to improve the understanding of geochemical cycling of U and their isotopic compositions in the riverine sediments that have been mixed with the influence of human activities.

The reservoir nearby a U metallurgical site in northern Guangdong Province, China offers an excellent location for studying U isotopic geochemistry in riverine sediments, where have been impacted by both anthropogenic activities and authigenic origin. Industrial activities of U mining and metallurgy had gave rise to the serious contamination of the aquatic system (Liu et al., 2015; Yin et al., 2019), apart from the widespread regional enrichments/pollution of toxic metal(loid)s in environmental media due to extensive and large scale industrial process (Liu et al., 2020; Wang et al., 2020, 2021). Recent studies have shown that U isotopes and geochemical approaches can trace U sources and processes controlling U mobility, and the potentially U isotopic fractionation induced by other processes needs to be considered (Dang et al., 2016; Dang et al., 2018a, b). For example, biotic reduction (U(VI)-to-U (IV)) can induce a significant U isotopic fractionation, with a preferential accumulation of the heavier ²³⁸U in the reduced species (Dang et al., 2016; Brown et al., 2018; Dang et al., 2018a, b). Adsorption on Mn/Fe oxides leads to ²³⁵U enrichment onto the surface of the oxides, while U (co)precipitation with phosphate has no isotopic fractionation (Brennecka et al., 2011; Dang et al., 2016). Understanding the processes that induce U isotopic fractionation is conducive to the insights into the U origin, accumulation, transport and fate in environmental media.

Herein, to systematically investigate the geochemical origin, enrichment and migration of U in a representative sedimentary core from a reservoir contaminated by uranium mill tailings, we apply novel and combined approaches, including (i) total and acid-leachable U contents of the sediments, (ii) U-Th isotopic composition, and (iii) U valence state and bonding form in selective sediments.

2. Materials and methods

2.1. Study area and sampling site

The studied area was within the catchment of a specific granitic U deposit, sited in the east of the Guidong granite massif, northern Guangdong Province, China. The U deposit is mainly consisted of medium-grained biotite granite, Early Jurassic porphyritic and Late Jurassic muscovite microgranite, with a U reserve of 1500-5000 tons (Yin et al., 2019). The uraniferous minerals are predominantly composed of pitchblende, pyrite, hydrogoethite, hematite, sphalerite and chlorite, with an average U content of 5-13 mg/kg (Liu et al., 2018). Ever since the discovery of the first U ore in 1957, U hydrometallurgical industry was established using heap leaching techniques with sulfuric acid (Yin et al., 2019). The solid and liquid wastes from mining and hydrometallurgical activities contained elevated levels of radionuclides as well as various harmful non-radioactive elements, leading to the concerns of environmental pollution. Herein, a representative sediment core located in a reservoir, was harvested to explore the geochemical cycling of U and its isotopic compositions.

Sediment core was obtained using a one-meter gravity corer in July 2012 from a reservoir, which is downstream the UMT site about 5 km and with overlying water of 10–15 m depth. Subsequently, it was cut into sub-samples of 10 mm length by a stainless steel blade and stored in pre-cleaned plastic bags. The sediment specimens were dried at room temperature and ground into powder (< 100 mm) by an agate mortar before chemical procedures. In addition, surface water along the stream/river that received the UMT leachate and water from different depth of the reservoir were collected and stored in 250 ml acid-cleaned polyethylene bottles after being acidulated by HNO₃.

2.2. Measurement of total U and accompanying elements in sediment and water

Approximately 100 mg of sediment samples and certain amounts of 68% HNO₃ and 48% HF (ν/ν) were mixed to digest, which were performed on a hot plate of 150 °C. This process was repeated for several times until a clear solution was obtained. After evaporating to remove additional HF, all samples were dissolved in 2% HNO₃ for measurement. Digestive solutions were filtered by 0.45 µm nylon membrane filters before measurement. Concentrations of U and associated metals (Cu, Zn



Fig. 1. Schematic illustration of U distribution in the receiving river of UMT leachate. The U concentration of leachates was cited from Liu et al. (2012).

and Pb) in the sediment and water samples were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) (Optima 7000 DV, PerkinElmer, Inc., Waltham, USA) according to the previous procedures reported by Wang et al. (2012). Duplicate samples, certified reference materials (GBW07406) and blank control were performed in the same way to ensure accuracy, which was found to be within 5% RSD. All of the reagents were of ultrapure grade (Sinopharm Chemical Reagent Co., China).

2.3. Acid leachable fraction analysis

Acid leachable fraction was extracted to examine the migration capacity of metals from sediments with a single-step extraction scheme. 0.25 g of sediment samples after air drying and grinding were taken for interacting with 0.5 M HCl (5 ml), which is required to last for 1 h and was subsequently centrifuged. The supernatant was obtained by centrifuging at 4000 rpm, which was then filtered by nylon membrane filters (0.45 μ m). Metal concentrations in supernatant were measured by ICP-OES. The results of determination are reliable, as the accuracy of a standard reference material (GBW07405, National Research Center for Certified Reference Materials, Beijing, China) was generally better than 5%.

2.4. U and Th isotopic compositions measurement

Sediments with appropriate amount were digested by HNO₃ and HF, which were then dissolved by 1% HNO₃ and spiked with a tracer (²²⁹Th-233–236 U) after evaporating. Ultrapure reagents obtained from Seastar Chemicals were used in the all chemical operations, which were conducted in a clean room (Shen et al., 2003). Prior to separation, Fe³⁺ solution was added to enrich U and Th by co-precipitation. Separated U and Th fractions were obtained with BioRad 1-X8 (100–200 mesh, 0.6–1.0 ml column volume), which is an anion exchange resin (Shen et al., 2002). Then, U and Th fractions were dried and then dissolved in 1% HNO₃ (+ 0.1% HF) for instrumental analysis.

The isotopic compositions of U and Th were determined on a multi-

collector inductively coupled plasma mass spectrometer, Thermo Scientific Neptune (Shen et al., 2012; Cheng et al., 2013). Before measurement, dilute HNO₃ was adopted to physically wash the spray chamber and micro-nebulizer for removing the contamination caused by previous samples (Shen et al. 2002), and desolvation introduction techniques was introduced to increase transmission efficiency (Shen et al., 2012; Cheng et al. 2013). Isotopic compositions of U (δ^{238} U) in the sediments is presented 238 U/ 235 U value relative to that of CRM-112A (atomic ratio, 137.832 ± 0.015), which is calculated by Eq. (1). Detailed illustration about operating conditions and data acquisition/calculation had been described in previous studies (Cheng et al. 2013; Shen et al. 2012).

$$\delta^{238}U = \left[\frac{\binom{238}{U}}{\binom{238}{235}} U_{\text{sample}}^{235} - 1\right] \times 1000 \tag{1}$$

In addition, to assess U contributions from detrital/authigenic sources, all samples were analyzed systematically for their 234 U/ 238 U ARs. 234 U/ 238 U ARs. 234 U/ 238 U ARs were calculated from the equation of 234 U/ 238 U atomic ratios as *Eq.* (2), where δ^{234} U is the 234 U/ 238 U atomic ratio relative to that of U isotopic standard (Cheng et al., 2013).

 δ^{234} U = (²³⁴U/²³⁸U ÅR-1) × 1000 (2).

2.5. XPS and EXAFS analysis

Chemical state of Fe in sediment was measured on X-ray photoelectron spectroscopy (XPS, Thermo Fisher K-alpha), and obtained spectra were analyzed by Thermo Scientific Advantage software (Liu et al., 2021). Charge correcting was conducted using the binding energy (BE) of aliphatic carbon (284.8 eV) from C 1 s line. A spin-orbit splitting of 13.1 eV and satellite peaks of Fe^{2+} and Fe^{3+} were used for fitting Fe 2p spectra, and the proportions of Fe^{2+} and Fe^{3+} were calculated by respective peak areas (Yamashita and Hayes, 2008).

Extended X-ray absorption fine structure (EXAFS) of U L_{III}-edge was determined at Shanghai Synchrotron Radiation Facility (BL14W, Shanghai, China). Obtained EXAFS spectra was processed by IFFEFIT



Fig. 2. The distribution of total content and acid-leachable content of U and Th in sedimentary profile.

7.0 software (Sheng et al., 2016; Sun et al., 2014; Song et al., 2018). The fitting results of coordination number (CN), interatomic distance (R), and Debye-Waller factor (σ^2) were reported. The fraction of U(VI) can be evaluated with the coordination number (CN) of U-O_{ax} shell, which is based on an assumption of U(VI) is in the form of UO₂²⁺ with 2 O_{ax} (O'Loughlin, et al., 2010; Sheng et al., 2014).

3. Results and discussion

3.1. Distinction of U enrichment

A systematic investigation of U distribution in the aqueous environment downstream the UMT disposal site was performed and schematically shown in Fig. 1. Notably, U concentrations (73-316 µg/L) in surface water collected along the receiving river/stream significantly exceed the limit value of Regulations for Radiation and Environmental Protection of Uranium Mining and Metallurgy (GB23727-2009) in China (50 µg/L), and show a remarkable decreasing trend with the distance away from the UMT disposal site. U concentration (3 µg/L) in surface water of the reservoir, which was about 5 km away from UMT, was found to be within the guideline range (2–15 μ g/L) proposed by the World Health Organization (WHO). However, an elevation of U concentration (ranging from 3 to 138 µg/L) was observed across the water column. The elevated U concentration found in the overlying water may suggest the potential of U release from the sediments. Therefore, a sedimentary core was collected from the reservoir to reveal the U enrichment mechanism and re-migration potential.

The total content and acid-leachable content of U and Th in sediments were exhibited in Fig. 2. Elevated U contents (207.3–1117.7 mg/ kg) were found in studied sediments as compared to sediments from other U mining/metallurgy impacting area (Kipp et al., 2009; Troyer et al., 2014; Stetten et al., 2018), which exhibited significant accumulation of U in the sediment profile. Relatively higher contents of U were found at the middle of the sedimentary core, while Th concentrations (74.7–131.5 mg/kg) were lower than U and with little variation, which could be ascribed to its inactive chemical property and poor migration capability (Kipp et al., 2009). The acid-leachable fraction, which includes the fraction of elements weakly adsorbed by sediments, incorporated by carbonate minerals and organic matter, was used to evaluate the capacity of pollutants re-migration (Ayyamperumal et al., 2006;



Fig. 3. Total U content and 234 U/ 238 U activity ratio (AR) as a function of depth of sedimentary profile.

Jayaprakash et al., 2014). The amount of acid-leachable U is of the order of 90.3–638.5 mg/kg, which constitutes up to 29.3–68.7% of total U content, suggesting a serious re-migration risk, especially at the middle depth. However, acid-leachable Th with an average content of 42.1 mg/kg and proportion of 38.0% does not vary with depth evidently.

3.2. Differentiation of U-Th isotopes

The distribution of ²³⁴U/²³⁸U ARs and total U contents of sedimentary profile are largely subject to depth variation, as depicted in Fig. 3. The measured ${}^{234}U/{}^{238}U$ ARs in these reservoir sediments show two distinct features, including the upper and middle parts (samples from W2 to W30) and the bottommost sediment (W42), where the U contents were in the range of 337.3-1117.7 mg/kg (average 683.3 mg/kg) and characterized with ²³⁴U/²³⁸U ARs that are slightly less than 1.0, indicating that a recent and gentle disequilibrium event might either preferentially mobilize 234U or 238U enrichment have occurred. On the contrary, the deeper part of the four consecutive sediments (from W31 to W34) and W39 are considerably enriched in ²³⁴U relative to ²³⁸U with an averaged ²³⁴U/²³⁸U AR of 1.01, which is the feature of lower U contents (245.0-299.1 mg/kg), indicating the bulk deficit of ²³⁸U or preferentially geochemical enrichment of ²³⁴U in near lowermost depths. Moreover, the upper part (samples from W2 to W10) exhibited elevated ²³⁴U/²³⁸U ARs in comparison with the immediate underlying sediment (samples from W11 to W17), where higher U contents were observed. It may indicate that, the diffusion of U from the middle layer to the upper layer under extreme hydrodynamic influence such as flood resulting in an increase of 234 U/ 238 U ARs in the upper part, which have also been observed in Skwarzec et al. (2002). As shown in Fig. 3, a clear upward trend of 234 U/ 238 U ARs as a function of depth was found at the middle layers (samples from W11 to W30), implying the ability of U in this segment to diffuse upwards decreases with depth. The distribution of $^{234}U/^{238}U$ ARs have confirmed that the U in the sedimentary profile is inclined to diffuse to the upper layer, which may be the reason for the U concentration in the overlying water column increasing with depth (Fig. 1).

There are several mechanisms contributing to the preferentially release of 234 U from the environmental matrix: (i) leaching from radiation-damaged sites, (ii) oxidation, and (iii) alpha recoil (Maher et al., 2006). 234 U-depleted matrix caused by direct ejection is only measurable in detrital grains, while non-detrital matter such as carbonates, iron oxides, organic matter and clay minerals are 234 U-rich



Fig. 4. Activity ratio variations of $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{234}\text{U}$ from secular equilibrium (intersection of the axes at activity ratios = 1.0) in the sedimentary profile from the reservoir. Error bars are quoted at the 2σ level.The results shown in region 1 and 2 are from the upper and middle parts (except for W42 deriving from deep segment) while that in Region 4 are from deeper parts.

(Andersson et al., 2001). Therefore, sediments with $^{234}\text{U}/^{238}\text{U}$ ARs being slightly < 1.0 are comprised of U arising from both detrital and non-detrital matter, and the contribution of detrital matter would be higher than that of non-detrital matter. In addition, ^{238}U enrichment is usually associated with the reduction of U. Therefore, it is still poorly constrained that $^{234}\text{U}/^{238}\text{U}$ AR < 1.0 observed in the specific layers is whether the consequence of detrital contributor outcompeting non-detrital part or U reduction.

Sub-sediments having 234 U/ 238 U AR > 1.0 are unexpected as the values of sediment solids are normally anticipated to be lower than unity. Numerous studies show that U isotopes can be readily sequestered by organic matters and amorphous ferromanganese oxyhydroxides (Berthelin et al., 1987; Dearlove et al., 1991; Yang and Edwards, 1984). In this study, we tend to believe that U adsorption from overlying water with 234 U/ 238 U AR > 1.0 onto non-detrital matter is reasonable, which could be later precipitated onto sediment grains in the fluvial system.

According to the study from Latham and Schwarcz (1987) and open-system empirical model (Rosholt, 1985), the U-Th isotopic features could be explained more specifically. As shown in Fig. 4, the deeper sediments except for W42 fell within the region 4 while other depth sediments lie in region 1 and 2. Sediments plotted in region 1 have the preference of removing ²³⁴U and ²³⁰Th enrichment. In particular, W19 indicates that ²³⁴Th alpha recoil is the predominant process leading to 234 U-loss (230 Th/ 234 U AR \approx 1.0); meanwhile, there is a preferential leaching of 234 U (234 U/ 238 U AR < 1.0) (Latham and Schwarcz, 1987). Samples from the surface layers (W2-W4) and the middle layers (W11–16) are categorized into region 2 in which 230 Th/ 234 U AR < 1.0 and 234 U/ 238 U AR < 1.0. It is well understood for 234 U/ 238 U AR < 1.0, while possible process leading to yield 230 Th/ 234 U AR < 1.0, might be concerned with U precipitation from overlying water/pore water, in which ²³⁴U concentrations are higher than authigenic ²³⁰Th, under possible hydrodynamic influence and indistinctive ²³⁴U removal (Latham and Schwarcz, 1987). For the near bottom sediments, the variation of 234 U/ 238 U ARs and 230 Th/ 234 U ARs falls into region 4 in which represents $^{234}U/^{238}U$ AR > 1.0 and $^{230}Th/^{234}U$ AR > 1.0, indicating the enrichment of ²³⁴U relative to ²³⁸U by alpha recoil injection (Kanai et al., 1998). The enriched ²³⁰Th might not only result from radioactive decay, but also from the uninterrupted contribution of indistinctive hydrogenous Th from the water column/pore water system; the latter could be attributed to the coexistence of hydrogenous Th and carbonates (Dean, 2014; Lin et al., 1996).

Table 1

Tuble 1		
Activity ratios of ²³⁴ U/ ²³⁸ U	232 Th/ 238 U and 230 Th	$/^{232}$ Th in sedimentary profile.

Sub-samples	234 _{U/} 238 _{U AR}	²³² Th/ ²³⁸ U AR	²³⁰ Th/ ²³² Th AR
W2	0.9900	0.2044	3.5226
W3	0.9857	0.1556	3.8135
W4	0.9861	0.1834	4.6679
W5	0.9882	0.2197	6.2388
W6	0.9890	0.1984	7.4742
W7	0.9945	0.1663	11.3607
W8	0.9919	0.1418	11.0043
W9	0.9828	0.0981	6.9285
W10	0.9883	0.1922	5.7960
W11	0.9807	0.0756	6.6891
W12	0.9758	0.0388	16.2989
W13	0.9762	0.0478	14.3151
W14	0.9781	0.0531	10.7130
W15	0.9799	0.0570	12.4692
W16	0.9817	0.0720	11.6106
W17	0.9834	0.0821	13.6525
W18	0.9810	0.0511	17.8349
W19	0.9789	0.0595	16.7286
W20	0.9851	0.0864	23.2781
W21	0.9827	0.0554	25.0469
W22	0.9846	0.0302	20.4604
W23	0.9883	0.0432	31.8711
W24	0.9879	0.0713	17.5954
W25	0.9874	0.0595	13.6583
W26	0.9930	0.0618	29.2423
W27	0.9896	0.0721	33.9716
W28	0.9956	0.0948	25.0217
W29	0.9911	0.0656	26.2012
W30	0.9936	0.0786	34.7406
W31	1.0090	0.2375	11.6292
W32	1.0140	0.2737	9.0273
W33	1.0184	0.3051	8.3551
W34	1.0212	0.3257	8.7867
W39	1.0201	0.2588	15.9416
W42	0.9868	0.0614	37.3928

3.3. Origin of the enriched U

The origin of U is classified into lithogenic and non-lithogenic U (Och et al., 2016). Lithogenic U is commonly found incorporated into minerals of detrital origin (granitoid rocks) (Dawood, 2010), while non-lithogenic U is deposited in sediments by co-precipitated with organic matter and iron oxide (McManus et al., 2005; Sani et al., 2004). We calculated ²³⁴U/²³⁸U, ²³²Th/²³⁸U and ²³⁰Th/²³²Th ARs to investigate the origin of U in a sedimentary core, and the distribution of these ratios were exhibited in Table 1. ²³²Th values were employed to evaluate the detrital input of Th to sediments (Robinson et al. 2008). ²³⁰Th/²³²Th ARs were further applied on the clarification of the predominant origin of Th (detrital or non-detrital origin), and to assess the contamination of ²³⁰Th (Yusoff, et al., 2015). Normal ²³⁰Th/²³²Th ARs in sediments range from 0.8 to 1.5 (demonstrating lithogenic origin), contamination can be identified when 230 Th/ 232 Th AR > 1.5 (San Miguel et al. 2004). In present study, all 230 Th/ 232 Th ARs were in excess of 1.5 and range between 3.5226 \pm 0.0102 and 37.3928 \pm 0.1093, indicating the contamination have apparently occurred as a result of being directly discharged of UMT leachate. In addition, sediments characterized by ²³²Th/²³⁸U AR > 1.0 indicate greater abundance of Th from detrital input, i.e., suggesting dominant lithogenic origins of U and Th (Yusoff and Mohamed, 2017). Sediments printed by 234 U/ 238 U AR < 1.0, 232 Th/ 238 U AR > 1.0 and $^{230}\text{Th}/^{232}\text{Th}\,\bar{\text{AR}}<1.0$ were not observed, which indicate that all the sediments are predominantly generated from non-lithogenic origin (Yusoff and Mohamed, 2017). Additionally, if sediments are primarily derived from detrital matter (characterized by preferential leaching of ²³⁴U), the magnitude of changes of ²³⁸U/²³⁵U should be positively correlated with those in ²³⁵U/²³⁴U (Brennecka et al., 2010). It was not observed in the sedimentary core (Fig. S1), indicating that the variations of these ratios were affected by U geochemical behaviors (typical of redox process and adsorption).



Fig. 5. Activity ratio variations of $^{230}\text{Th}/^{234}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$. Blue circles show that the ratios of $^{230}\text{Th}/^{234}\text{U}$ AR and $^{230}\text{Th}/^{238}\text{U}$ AR are higher than 1.0 and $^{230}\text{Th}/^{234}\text{U}$ AR $<^{230}\text{Th}/^{238}\text{U}$ AR; Red circles show that the ratios of $^{230}\text{Th}/^{234}\text{U}$ AR and $^{230}\text{Th}/^{238}\text{U}$ AR; Red circles show that the ratios of $^{230}\text{Th}/^{234}\text{U}$ AR and $^{230}\text{Th}/^{238}\text{U}$ AR; Red circles show that the ratio of $^{230}\text{Th}/^{234}\text{U}$ AR and $^{230}\text{Th}/^{238}\text{U}$ AR are higher than 1.0 and $^{230}\text{Th}/^{234}\text{U}$ AR $>^{230}\text{Th}/^{234}\text{U}$ AR are higher than 1.0 and $^{230}\text{Th}/^{234}\text{U}$ AR $>^{230}\text{Th}/^{238}\text{U}$ AR; Green circles are associated with $^{230}\text{Th}/^{234}\text{U}$ AR < 1.0, $^{230}\text{Th}/^{238}\text{U}$ AR < 1.0 and $^{230}\text{Th}/^{234}\text{U}$ AR $>^{230}\text{Th}/^{238}\text{U}$ AR (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

3.4. U enrichment mechanism

U/Th ARs were applied to unveil U enrichment mechanisms. Oxidized hexavalent U is the most common form and soluble in most natural waters (Langmuir, 1978), while Th is insoluble (Costa and McManus, 2017). The obvious discrepancy of solubility for Th and U leads to the fractionation of 230 Th from 234 U and 238 U. Therefore, ²³⁴U/²³⁸U ARs in natural waters usually lie in excess of unity, while their 230 Th/ 234 U and 230 Th/ 238 U ARs are substantially lower than unity (Plater et al., 1992). Correspondingly, ²³⁰Th/²³⁴U and ²³⁰Th/²³⁸U ARs in uncontaminated sediments are higher than 1.0. Moreover, $^{230}\mathrm{Th}/^{234}\mathrm{U}$ AR is larger than 230 Th/ 238 U AR, since the reactivity of 230 Th $\ll ^{238}$ U < 234 U (Plater, et al., 1992). As shown in Fig. 5, the values of 230 Th/ 234 U ARs and ²³⁰Th/²³⁸U ARs in most of the sub-sediments are higher than 1.0 and characterized by 230 Th/ 234 U > 230 Th/ 238 U (marked as red circle), indicating that anthropogenic activity did not mask the U/Th ARs of bedrock weathering. However, the nethermost sediments (except for W42) exhibit 230 Th/ 234 U AR < 230 Th/ 238 U AR (marked as blue circle), suggesting ²³⁴U accumulation from overlying water/pore water. Since ²³⁴U is more likely associated with U⁶⁺ (Pekala et al., 2009; Vargas et al., 1995), U adsorption maybe the dominant process causing U enrichment observed in these sub-sediments. Notably, sediments characterized by $^{230} Th/^{234} U$ AR and $^{230} Th/^{238} U$ AR < 1.0 and $^{230} Th/^{234} U$ AR > ²³⁰Th/²³⁸U AR are also observed (marked as green circle), which may owe to the effects of extreme U input from the water column. Since the values of ²³⁴U/²³⁸U ARs in water column are usually higher than 1.0, the input of U from overlying water would result in 230 Th/ 234 U < 230 Th/ 238 U; the opposite result shown in Fig. 5 indicates 238 U enrichment and/or preferential removal of 234U after U precipitation. The preferential removal of ²³⁴U is likely to occur, since U in sediments tends to migrate upward as discussed above (Section 3.2), while the ²³⁸U enrichment needs to be confirmed.

 δ^{238} U was further investigated to illustrate U accumulation mechanisms. To enhance the understanding of the variability of δ^{238} U value in U ores and sediment/water contaminated by U ore exploitation, δ^{238} U values normalized to CRM-112A were compiled and graphically summarized in Fig. 6. Clearly, δ^{238} U values in different ores varied from - 0.75–2.41‰ (Uvarova et al., 2014). It is evident that δ^{238} U values in all water samples (i.e., sea water, lake water and river water) lie between

− 0.81‰ and 0.31‰, with the heaviest value in sea water (Montoya-Pino et al. 2010) and the lightest one in lake water (Wang et al., 2019). δ^{238} U values in the studied sediment profile ranged from – 0.6166 ± 0.0076‰ to – 0.0370 ± 0.0065‰, with the largest variance of 0.5796‰. In comparison, the variation of δ^{238} U values observed in other surface freshwater sediments was – 0.6524 to 0.2167‰ with the maximum variance reaching at 0.8690‰ (Dang et al., 2018a), which concluded that biotic reduction contributes to the extremely U isotopic fractionation. Meanwhile, δ^{238} U values in sedimentary cores under seasonal anoxia and permanently anoxic conditions ranges from – 0.4275 to – 0.1663‰ (maximum variance: $\Delta \delta^{238}$ U = 0.4140‰), respectively (Wang et al., 2019), which clearly indicates that the anoxic condition can lead to a larger U isotopic fractionation.

Actually, δ^{238} U of the sedimentary profile is the combination of contributions from the bedrock weathering (natural activity) and UMT leachate (anthropogenic activity) and subsequent biogeochemical processes. If the δ^{238} U of sediments is only a mixture of natural and anthropogenic sources, a positive correlation between δ^{238} U and acidleachable U fraction can be observed according to the binary mixing equation/line (Eq. (3)), since this fraction of U basically comes from anthropogenic source (Javaprakash et al., 2008). If not, it tends to suggest that the presence of biogeochemical processes may contribute to the fractionation of δ^{238} U. As displayed in Fig. 7, δ^{238} U_{measured} and acid-leachable U contents were not positively correlated, which can be explained by biogeochemical fractionation of U. To clarify the dominant mechanism leading to U isotopic fractionation, the acid-leachable U fraction as a substitution for the contribution rate of UMT was applied, aiming to calculate the U isotopic composition (marked as δ^{238} U_{calcul} $_{lated}$) from the mixing of UMT and bedrock weathering. If $\delta^{238}U_{measured}$ is higher than $\delta^{238} U_{calculated}$, indicating the occurrence of biotic reduction (Basu et al., 2014; Dang et al., 2016). Conversely, U adsorption would lead to $\delta^{238} U_{measured}$ lower than $\delta^{238} U_{calculated}$, since U adsorption on Fe/Mn minerals would induce the accumulation of light isotope (^{235}U) in the solid phase (Dang et al., 2016), while ²³⁸U tends to be enriched in reductive phases (U^{4+}) (Basu et al., 2014).

$$S^{i}_{UMT} = \frac{(\delta^{238}U)_{i} - (\delta^{238}U)_{nat.}}{(\delta^{238}U)_{UMT} - (\delta^{238}U)_{nat.}} \times 100$$
(3)

Where $(\delta^{238}U)_i$, $(\delta^{238}U)_{UMT}$ and $(\delta^{238}U)_{nat.}$ are U isotopic composition of sediment *i*, uranium mill tailings (UMT, anthropogenic activity) and bedrock weathering (natural activity), respectively; S^i_{UMT} represents the contribution rate of UMT, which has been replaced with the acid-leachable U fraction in this study.

Sediments were classified into three categories based on the results of ²³⁰Th/²³⁴U ARs and ²³⁰Th/²³⁸U ARs, and marked as three different colors (Fig. 5). Fig. 7 shows that sediments with blue circle present the lowest acid-leachable U fraction, while the corresponding δ^{238} U_{measured} are not the lowest and higher than its δ^{238} U_{calculated}, indicating the fact that U reduction occurred. This fact can be further confirmed by the EXAFS results, where 47% of U in W39 has been found as U^{4+} (Fig. 8 and Table 2). According to the analysis of ²³⁰Th/²³⁴U ARs and ²³⁰Th/²³⁸U ARs, U adsorption is also believed to have occurred in these sediments (marked as blue circle). If U in these sediments was predominantly adsorbed by Fe/Mn minerals, which will lead to a fractionation magnitude of 0.2–0.4‰ (Dang et al., 2016), more negative δ^{238} U values should be observed in these sediments than other sediments. Therefore, U in sediments (blue circle) were not primarily adsorbed by Fe/Mn minerals but clay minerals, which can be further validated by EXAFS analysis, where U-Al signal was observed (Fig. 8 and Table 2). Sediments marked as green circle, with the feature of 230 Th/ 234 U AR < 1.0, 230 Th/ 238 U AR < 1.0 and 230 Th/ 234 U AR > 230 Th/ 238 U AR, imply the accumulation of ²³⁸U. To test the speculation of ²³⁸U accumulation, representative sub-sediments (W2 and W22) were selected to perform EXAFS and XPS analysis. It was found that the proportion of U^{4+} and

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Fig. 6. Comparison of U isotopic composition (δ^{238} U) among different samples (U ores, sediments and waters). All values have been renormalized to CRM-112A.



Fig. 7. Variations of δ^{238} U_{measured}, δ^{238} U_{calculated}, and acid-leachable U fraction as a function of depth in sedimentary profile; the color of the symbol for δ^{238} U_{measured} corresponds to the sediments with the same color exhibited in **Fig. 5**(For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

Fe²⁺ in W22 are 29% and 23.0%, respectively, both are higher than that in W2 (U⁴⁺: 16%, Fe²⁺: 20.2%). This result demonstrates that U reduction plays a pivotal role in ²³⁸U enrichment observed in sediments labeled as green circle, and more obvious U reduction would emerge in deeper sediments. Notably, the δ^{238} U_{measured} of W22 is far lower than its δ^{238} U_{calculated}, which may indicates the co-occurrence of U adsorption on Fe/Mn minerals, since ²³⁵U is prone to accumulate on these minerals. Additionally, acid-leachable U fraction of W22 is 56.8%, which is much larger than W39 (33.0%), but its δ^{238} U_{measured} is much lower than W39, indicating that U reduction occurring in W39 is stronger than W22, while U adsorption on Fe/Mn minerals is dominant in W22. Which can also be proved by the proportion of U⁴⁺ revealed by EXAFS characterizations (Fig. 8 and Table 2) and Fe²⁺ determined by XPS (Fig. 9).

Likewise, sub-sediments of W3 and W11 displayed the maximum and minimum $\delta^{238} U_{\text{measured}}$ value in the studied profile, respectively. If the δ^{238} U_{measured} values are only composed of the natural and anthropogenic sources, the $\delta^{238} U_{measured}$ of W11 should be larger than W3 because the acid-leachable U fraction of W11 is higher than W3. However, the opposite result indicates that the U reduction magnitude of W3 is greater than W11. As for sediments marked as red circle, W21 has the highest acid-leachable U fraction, whereas the largest $\delta^{238} U_{measured}$ value appears in W5. It is important to note that W5 contains higher amount of acid-leachable U fraction and larger $\delta^{238}U_{measured}$, and its U reduction magnitude is assumed to be even stronger than W39, which had been proved to be dominated by U reduction process according to the combined results of δ^{238} U_{measured}, EXAFS and XPS analysis. The bottommost layer (W42), where an abruptly increase of acid-leachable U was observed, exhibits similar $\delta^{238}U_{measured}$ and $\delta^{238}U_{calculated}$ value. It indicated that, U isotopic fractionation derived from U biogeochemical behaviors was not obvious in the bottommost layer, or the fractionation caused by U reduction had counteracted that by U adsorption. Therefore, U enrichment in the different depths of the profile was dominated by multiple mechanisms, including U adsorption and reduction, which can be well identified by ²³⁰Th/²³⁴U ARs, ²³⁰Th/²³⁸U ARs and respective δ^{238} U values.



Fig. 8. Raw data (a, b, c) and U-L_{III}-edge k^3 -weighted $\chi(k)$ data (d, e, f) and the corresponding Fourier transformed EXAFS data (g, h, i) of sediments from surface (W2), middle (W22) and bottom layer (W39).

 Table 2

 The fitted structural parameters of U-L_{III}-edge EXAFS spectra

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Subsamples	U ⁶⁺	U^{4+}	Shell	R (Å)	CN	σ^2 (Å ²)
W2	84%	16%	U-O _{ax}	1.74(1)	1.68(1)	0.021
			U-O1	2.35(2)	7.32(5)	0.027
			U-Al	3.62(4)	1.84(3)	0.035
W22	71%	29%	U-O _{ax}	1.72(3)	1.42(2)	0.019
			U-O1	2.34(1)	7.54(3)	0.028
			U-Al	3.61(4)	1.92(3)	0.031
W39	53%	47%	U-O _{ax}	1.75(1)	1.06(1)	0.023
			U-O1	2.34(2)	7.73(1)	0.027
			U-Al	3.63(3)	1.89(4)	0.034

Note: R is interatomic distance, CN is coordination number, σ^2 is the Debye Waller factor. The fraction of U^{6+} can be evaluated with the coordination number (CN) of U-O_{ax} shell, which is based on an assumption that U^{6+} is in the form of $UO_{2^+}^{2+}$ with 2 O_{ax}.

4. Conclusions

- (1) Extremely U contamination (207.3–1117.7 mg/kg) and remigration capacity (acid-leachable U fraction: 29.3–68.7%) were observed in 41 sediments from a representative depth profile of a reservoir, which links to the river of receiving leachates from uranium mill tailings.
- (2) It is often very difficult to discriminate the U isotopic fractionation, which is the combined result of source mixing (natural and anthropogenic origins) and biogeochemical fractionation (authigenic formation). However, our results suggest that U and Th isotopic ARs, U isotopic composition (δ^{238} U) and geochemical analysis can be used to uncover U enrichment mechanisms in 35 sediments with specific depth.
- (3) The revelation of main enrichment mechanisms (reduction or adsorption) of U in sediments with isotopic perspective is also very useful for the assessment of stability/release risk of U in environmental media.

This work provides a preliminary and critical practice of applying U-Th isotopes in the study of U geochemical behaviors and enrichment mechanism, and the theoretic framework based on field investigation data needs further test and development with more scenarios in future.

CRediT authorship contribution statement

Jin Wang: Writing - Original Draft, Conceptualization, Methodology, Formal analysis, Investigation, Funding acquisition and Project administration. Meiling Yin: Writing - Review & Editing, Formal analysis, Visualization and Investigation. Juan Liu: Editing. Chuan-Chou Shen: Writing - Review & Editing, Methodology. Tsai-Luen Yu: Methodology. Hong-Chun Li: Methodology, Writing - Review & Editing. Qiaohui Zhong: Writing - Review & Editing. Guodong Sheng: Methodology, Writing - Review & Editing. Ke Lin: Writing - Review & Editing. Xiuyang Jiang: Editing. Hongliang Dong: Methodology. Siyu Liu: Editing. Tangfu Xiao: Writing - Review & Editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.



Fig. 9. Fe 2p 3/2 spectra of sediments from surface (W2), middle (W22) and bottom layer (W39). Experimental data are discrete points and fitted curves are solid lines.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2021.125466.

References

- Andersson, P.S., Porcelli, D., Gustafsson, Ö., Ingri, J., Wasserburg, G.J., 2001. The importance of colloids for the behavior of uranium isotopes in the low-salinity zone of a stable estuary. Geochim. Et. Cosmochim. Acta 65, 13–25.
- Ayyamperumal, T., Jonathan, M.P., Srinivasalu, S., Armstrong-Altrin, J., Ram-Mohan, V., 2006. Assessment of acid leachable trace metals in sediment cores from river Uppanar. Cuddalore. southeast coast of India. Environ. Pollut. 143. 34–45.
- Basu, A., Sanford, R.A., Johnson, T.M., Lundstrom, C.C., Löffler, F.E., 2014. Uranium isotopic fractionation factors during U(VI) reduction by bacterial isolates. Geochim. Et. Cosmochim. Acta 136, 100–113.
- Basu, A., Brown, S.T., Christensen, J.N., DePaolo, D.J., Reimus, P.W., Heikoop, J.M., Woldegabriel, G., Simmons, A.M., House, B.M., Hartmann, M., Maher, K., 2015. Isotopic and geochemical tracers for U(VI) reduction and U mobility at an in situ recovery U mine. Environ. Sci. Technol. 49, 5939–5947.
- Berthelin, J., Gueniot, B., Munier-Lamy, C., 1987. An in situ experimental bag method to study the influence of environmental factors on uranium mobilization and preconcentration in soils. Uranium 3, 343–352.
- Bone, S.E., Dynes, J.J., Cliff, J.B., Bargar, J.R., 2017. Uranium(IV) adsorption by natural organic matter in anoxic sediments. Proc. Natl. Acad. Sci. USA 114, 711–716.
- Bopp, C.J., Lundstrom, C.C., Johnson, T.M., Sanford, R.A., Long, P.E., Williams, K.H., 2010. Uranium ²³⁸U/²³⁵U isotopic ratios as indicators of reduction: results from an in situ biostimulation experiment at Rifle, Colorado, U.S.A. Environ. Sci. Technol. 44, 5927–5933.
- Brennecka, G., Wasylenki, L.E., Weyer, S., Anbar, D.A., 2011. Uranium isotope fractionation during adsorption to Mn-Oxyhydroxides. Environ. Sci. Technol. 45, 1370–1375.
- Brennecka, G.A., Borg, L.E., Hutcheon, I.D., Sharp, M.A., Anbar, A.D., 2010. Natural variations in uranium isotope ratios of uranium ore concentrates: understanding the ²³⁸U/²³⁵U fractionation mechanism. Earth Planet. Sci. Lett. 291, 228–233.
- Cheng, H., Edwards, R.L., Shen, C.-C., Polyak, V.J., Asmerom, Y., Woodhead, J.D., Alexander, E.C., 2013. Improvements in ²³⁰Th dating, ²³⁰Th and ²³⁴U half-life values, and U-Th isotopic measurements by multi-collector inductively coupled plasma mass spectrometry. Earth Planet. Sci. Lett. 371–372, 82–91.
- Costa, K., McManus, J., 2017. Efficacy of ²³⁰Th normalization in sediments from the Juan de Fuca Ridge, northeast Pacific Ocean. Geochim. Et. Cosmochim. Acta 197, 215–225.
- Crawford, S.E., Lofts, S., Liber, K., 2017. The role of sediment properties and solution pH in the adsorption of uranium(VI) to freshwater sediments. Environ. Pollut. 220, 873–881.
- Cumberland, S.A., Grant, D., Grice, K., Moreau J., W., 2016. Uranium mobility in organic matter-rich sediments: a review of geological and geochemical processes. Earth-Sci. Rev. 159, 160–185.
- Cumberland, S.A., Etschmann, B., Brugger, J., Douglas, G., Evans, K., Fisher, L., Kappen, P., Moreau, J.W., 2018. Characterization of uranium redox state in organicrich Eocene sediments. Chemosphere 194, 602–613.
- Dang, D.H., Novotnik, B., Wang, W., Georg, R.B., Evans, R.D., 2016. Uranium isotope fractionation during adsorption, (co) precipitation, and biotic reduction. Environ. Sci. Technol. 50, 12695–12704.
- Dang, D.H., Wang, W., Pelletier, P., Poulain, A.J., Evans, R.D., 2018a. Uranium dispersion from U tailings and mechanisms leading to U accumulation in sediments: insights from biogeochemical and isotopic approaches. Sci. Total Environ. 610, 880–891.
- Dang, D.H., Evans, R.D., Wang, W., Omanović, D., Houssainy, A.E., Lenoble, V., Mullot, J.U., Mounier, S., Garnier, C., 2018b. Uranium isotope geochemistry in modern coastal sediments: Insights from Toulon Bay, France. Chem. Geol. 481, 133–145.
- Dawood, Y., 2010. Factors controlling uranium and thorium isotopic composition of the streambed sediments of the River Nile, Egypt. J. King Abdulaziz Univ. -Earth Sci. 21, 77–103.
- Zhao, D., Wang, X., Yang, S., Guo, Z., Sheng, G., 2012. Impact of water quality
- parameters on the sorption of U(VI) onto hematite. J. Environ. Radioact. 103, 20–29. Dean, J.R., 2014. Stable isotope analysis and U-Th dating of late glacial and Holocene lacustrine sediments from central Turkey. Ph.D. thesis of the University of Nottinepham.
- Dearlove, J.P.L., Longworth, G., Ivanovich, M., Kim, J.I., Delakowitz, B., Zeh, P., 1991. A study of groundwater-colloids and their geochemical interactions with natural radionuclides in Gorleben aquifer systems. Radiochim. Acta 52, 83–90.
- Fuller, A.J., Leary, P., Gray, N.D., Davies, H.S., Mosselmans, J.F.W., Cox, F., Law, G.T.W., 2020. Organic complexation of U(VI) in reducing soils at a natural analogue site: Implications for uranium transport. Chemosphere 254, 126859.
- Gilleaudeau, G.J., Romaniello, S.J., Luo, G., Kaufman, A.J., Zhang, F., Klaebe, R.M., Kah, L.C., Azmy, K., Bartley, J.K., Zheng, W., Knoll, A.H., Anbar, A.D., 2019. Uranium isotope evidence for limited euxinia in mid-Proterozoic oceans. Earth Planet. Sci. Lett. 521, 150–157.

- Greenwood, P., Brocks, J., Grice, K., Schwark, L., Jaraula, C., Dick, J., Evans, K., 2013. Organic geochemistry and mineralogy: I. Characterisation of organic matter associated with metal deposits. Ore Geol. Rev. 1–27.
- Jayaprakash, M., Jonathan, M.P., Srinivasalu, S., Muthuraj, S., Ram-Mohan, V., Rajeshwara-Rao, N., 2008. Acid-leachable trace metals in sediments from an industrialized region (Ennore Creek) of Chennai City, SE coast of India: an approach towards regular monitoring. Estuar., Coast. Shelf Sci. 76, 692–703.
- Jayaprakash, M., Viswam, A., Gopal, V., 2014. Bioavailable trace metals in micro-tidal Thambraparani estuary, Gulf of Mannar, SE coast of India. Estuar., Coast. Shelf Sci. 146, 42–48.
- Kanai, Y., Okuyama, Y., Seo, T., Sakamaki, Y., 1998. Geochemical micro-behavior of natural U-series nuclides in granitic conglomerate from the Tono mine, central Japan. Geochem. J. 32, 351–366.
- Kipp, G.G., Stone, J.J., Stetler, L.D., 2009. Arsenic and uranium transport in sediments near abandoned uranium mines in Harding County, South Dakota. Appl. Geochem. 24, 2246–2255.
- Langmuir, D., 1978. Uranium solution-mineral equilibria at low temperatures with applications to sedimentary ore deposits. Geochim. Et. Cosmochim. Acta 42, 547–569.
- Latham, A.G., Schwarcz, H.P., 1987. On the possibility of determining rates of removal of uranium from crystalline igneous rocks using U-series disequilibria—1: a U-leach model, and its applicability to whole-rock data. Appl. Geochem. 2, 55–65.
- Latta, D.E., Kemner, K.M., Mishra, B., Boyanov, M.I., 2016. Effects of calcium and phosphate on uranium(IV) oxidation: comparison between nanoparticulate uraninite and amorphous UIV–phosphate. Geochim. Et. Cosmochim. Acta 174, 122–142.
- Lau, V., Lyons, K., W, T, Maher, K., 2020. Uranium reduction and isotopic fractionation in reducing sediments: insights from reactive transport modeling. Geochim. Et. Cosmochim. Acta 287, 65–92.
- Lin, J.C., Broecker, W.S., Anderson, R.F., Hemming, S., Rubenstone, J.L., Bonani, G., 1996. New ²³⁰Th/U and ¹⁴C ages from Lake Lahontan carbonates, Nevada, USA, and a discussion of the origin of initial thorium. Geochim. Et. Cosmochim. Acta 60, 2817–2832.
- Liu, J., Li, H., Wang, J., Song, G., Qi, J., Chen, Y., Li, P., Wu, Y., 2012. Environmental quality of surface waters in a uranium industrial site in South China. Environ. Chem. 31, 981–989 (in Chinese with English abstract).
- Liu, J., Ren, S., Cao, J., Tsang, D., Beiyuan, J., Peng, Y., Fang, F., She, J., Yin, M., Shen, N., Wang, J., 2021. Highly efficient removal of thallium in wastewater by MnFe₂O₄biochar composite. J. Hazard. Mater. 401, 123311.
- Liu, J., Wang, J., Li, H., Shen, C.C., Chen, Y., Wang, C., Ye, H., Long, J., Song, G., Wu, Y., 2015. Surface Sediment Contamination by Uranium Mining/Milling Activities in South China. CLEAN - Soil Air Water 43, 414–420.
- Liu, J., Luo, X., Wang, J., Xiao, T., Yin, M., Belshaw, N.S., Linghu, W., 2018. Provenance of uranium in a sediment core from a natural reservoir, South China: application of Pb stable isotope analysis. Chemosphere 193, 1172–1180.
- Liu, J., Zhou, Y., She, J., Tsang, D., Lippold, H., Wang, J., Jiang, Y., Wei, X., Yuan, W., Luo, X., Zhai, S., Song, L., 2020. Quantitative isotopic fifingerprinting of thallium associated with potentially toxic elements (PTEs) in fifluvial sediment cores with multiple anthropogenic sources. Environ. Pollut. 266, 115252.
- Maher, K., Steefel, C.I., DePaolo, D.J., Viani, B.E., 2006. The mineral dissolution rate conundrum: insights from reactive transport modeling of U isotopes and pore fluid chemistry in marine sediments. Geochim. Et. Cosmochim. Acta 70, 337–363.
- McManus, J., Berelson, W., Klinkhammer, G., Hammond, D., Holm, C., 2005. Authigenic uranium: relationship to oxygen penetration depth and organic carbon rain. Geochim. Et. Cosmochim. Acta 69, 95–108.
- Montoya-Pino, C., Weyer, S., Anbar, A.D., Pross, J., Oschmann, W., Schootbrugge, B.V. D., Arz, H.W., 2010. Global enhancement of ocean anoxia during oceanic anoxic event 2: a quantitative approach using U isotopes. Geology 38, 315–318.
- Murphy, M.J., Stirling, C.H., Kaltenbach, A., Turner, S.P., Schaefer, B.F., 2014. Fractionation of 238U/235U by reduction during low temperature uranium mineralisation processes. Earth Planet. Sc. Lett. 388, 306–317.
- Och, L.M., Müller, B., Marz, C., Wichser, A., Vologina, E.G., Sturm, M., 2016. Elevated uranium concentrations in Lake Baikal sediments: burial and early diagenesis. Chem. Geol. 441, 92–105.
- O'Loughlin, E.J., Kelly, R.D., Kemner, R.M., 2010. XAFS investigation of the interactions of U(VI) with secondary mineralization products from the bioreduction of Fe(III) oxides. Environ. Sci. Technol. 44, 1656–1661.
- Pękala, M., Kramers, J.D., Waber, H.N., Gimmi, T., Alt-Epping, P., 2009. Transport of ²³⁴U in the opalinus clay on centimetre to decimetre scales. Appl. Geochem. 24, 138–152.
- Plater, A.J., Ivanovich, M., Dugdale, R.E., 1992. Uranium series disequilibrium in river sediments and waters: the significance of anomalous activity ratios. Appl. Geochem. 7, 101–110.
- Robinson, L.F., Noble, T.L., Mcmanus, J., 2008. Measurement of adsorbed and total ²³²Th/²³⁰Th ratios from marine sediments. Chem. Geol. 252, 169–179.
- Rosholt, 1985. Uranium-trend systematics for dating quaternary sediments. United states department of the interior geological survey. Open-File Rep. 85–298.
- San Miguel, E.G., Boliver, J.P., Garcia-Tenorio, R., 2004. Vertical distribution of Thisotope ratios, ²¹⁰Pb, ²²⁶Ra and ¹³⁷Cs in sediment cores from an estuary affected by anthropogenic releases. Sci. Total Environ. 318, 143–157.
- Sani, R.K., Peyton, B.M., Amonette, J.E., Geesey, G.G., 2004. Reduction of uranium(VI) under sulfate-reducing conditions in the presence of Fe(III)-(hydr)oxides. Geochim. Et. Cosmochim. Acta 68, 2639–2648.
- Scott, T.B., Allen, G.C., Heard, J.P., Randell, G.M., 2005. Reduction of U(VI) to U(IV) on the surface of magnetite. Geochim. Et. Cosmochim. Acta 69, 5639–5646.

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- Selvakumar, R., Ramadoss, G., Mridula, P.M., Rajendran, K., Thavamani, P., Ravi, N., Megharaj, M., 2018. Challenges and complexities in remediation of uranium contaminated soils: a review. J. Environ. Radioact. 192, 592–603.
- Shen, C.-C., Edwards, R.L., Cheng, H., Dorale, J.A., Edmonds, H.N., 2002. Uranium and thorium isotopic and concentration measurements by magnetic sector inductively coupled plasma mass spectrometry. Chem. Geol. 185, 165–178.
- Shen, C.-C., Cheng, H., Edwards, R.L., Moran, S.B., Edmonds, H.N., Hoff, J.A., Thomas, R. B., 2003. Measurement of attogram quantities of ²³¹Pa in dissolved and particulate fractions of seawater by isotope dilution thermal ionization mass spectroscopy. Anal. Chem. 75, 1075–1079.
- Shen, C.-C., Wu, C.-C., Cheng, H., Edwards, R.L., Hsieh, Y.-T., Gallet, S., Chang, C.-C., Li, T.-Y., Lam, D.D., Kano, A., Hori, M., Spötl, C., 2012. High-precision and highresolution carbonate ²³⁰Th dating by MC-ICP-MS with SEM protocols. Geochim. Et. Cosmochim. Acta 99, 71–86.
- Sheng, G., Shao, X., Li, Y., Li, J., Dong, H., Cheng, W., Gao, X., Huang, Y., 2014. Enhanced removal of uranium(VI) by nanoscale zerovalent iron supported on na-bentonite and an investigation of mechanism. J. Phys. Chem. A 118, 2952–2958.
- Sheng, G.D., Yang, P.J., Tang, Y.N., Hu, Q.Y., Li, H., Ren, X.M., 2016. New insights into the primary roles of diatomite in the enhanced sequestration of UO²⁺₂ by zerovalent iron nanoparticles: an advanced approach utilizing XPS and EXAFS. Appl. Catal. B Environ. 193, 189–197.
- Skwarzec, B., Boryło, A., Struminska, D., 2002. ²³⁴U and ²³⁸U isotopes in water and sediments of the southern Baltic. J. Environ. Radioact. 61, 345–363.
- Song, W., Wang, X., Chen, Z., Sheng, G., Hayat, T., Wang, X., 2018. Enhanced immobilization of U(vi) on mucor circinelloides in presence of As(v): batch and XAFS investigation. Environ. Pollut. 237, 228–236.
- Stetten, L., Mangeret, A., Brest, J., Sedercolomina, M., Pape, P.L., Ikogou, M., Morin, G., 2018. Geochemical control on the reduction of U(VI) to mononuclear U(IV) species in lacustrine sediments. Geochim. Et. Cosmochim. Acta 222, 171–186.
- Stylo, M., Neubert, N., Wang, Y., Monga, N., Romaniello, S.J., Weyer, S., Bernier-Latmani, R., 2015. Uranium isotopes fingerprint biotic reduction. Proc. Natl. Acad. Sci. USA 112, 5619–5624.
- Sun, Y., Li, J., Wang, X.J., 2014. The retention of uranium and europium onto sepiolite investigated by macroscopic, spectroscopic and modeling techniques. Geochim. Et. Cosmochim. Acta 140, 621–643.
- Tinnacher, R.M., Nico, P.S., Davis, J.A., Honeyman, B.D., 2013. Effects of fulvic acid on uranium(VI) sorption kinetics. Environ. Sci. Technol. 47, 6214–6222.
- Troyer, L.D., Stone, J.J., Borch, T., 2014. Effect of biogeochemical redox processes on the fate and transport of as and u at an abandoned uranium mine site: an x-ray absorption spectroscopy study. Environ. Chem. 11, 18–27.
- Uvarova, Y.A., Kyser, T.K., Geagea, M.L., Chipley, D., 2014. Variations in the uranium isotopic compositions of uranium ores from different types of uranium deposits. Geochim. Et. Cosmochim. Acta 146, 1–17.
- Vargas, M.J., Tome, F.V., Sanchez, A.M., 1995. Behaviour of uranium, thorium and ²²⁶Ra in surface waters from a river passing through a granitic region in the Southwest of Spain. Nucl. Geophys. 9, 567–578.

- Wang, J., Liu, J., Li, H., Song, G., Chen, Y., Xiao, T., Qi, J., Zhu, L., 2012. Surface Water Contamination by Uranium Mining/Milling Activities in Northern Guangdong Province, China. CLEAN - Soil, Air, Water 40, 1357–1363.
- Wang, J., Jiang, Y., Sun, J., She, J., Yin, M., Fang, F., Xiao, T., Song, G., Liu, J., 2020. Geochemical transfer of cadmium in river sediments near a lead-zinc smelter. Ecotoxicol. Environ. Saf. 196, 110529.
- Wang, J., Liu, J., Chen, Y., Song, G., Chen, D., Xiao, T., Li, H., Wang, C., Jiang, F., 2016. Preliminary results of spatial distribution of uranium and thorium in soil profiles near a uranium industrial site, Guangdong province, China. Nukleonika 61, 367–371.
- Wang, J., Liu, J., Li, H., Chen, Y., Xiao, T., Song, G., Chen, D., Wang, C., 2017. Uranium and thorium leachability in contaminated stream sediments from a uranium minesite. J. Geochem. Explor. 176, 85–90.
- Wang, W., Dang, D.H., Novotnik, B., Phan, T.T., Evans, R.D., 2019. Variations in U concentrations and isotope signatures in two Canadian lakes impacted by U mining: a combination of anthropogenic and biogeochemical processes. Chem. Geol. 506, 58–67.
- Wang, J., Wang, L., Wang, Y., Tsang, D., Yang, X., Beiyuan, J., Yin, M., Xiao, T., Jiang, Y., Lin, W., Zhou, Y., Liu, J., Wang, L., Zhao, M., 2021. Emerging risks of toxic metal (loid)s in soil-vegetables infifluenced by steel-making activities and isotopic source apportionment. Environ. Int. 146, 106207.
- Weyer, S., Anbar, A.D., Gerdes, A., Gordon, G.W., Algeo, T.J., Boyle, E.A., 2008. Natural fractionation of U-238/U-235. Geochim. Et. Cosmochim. Acta 72, 345–359.
- Yamashita, T., Hayes, P., 2008. Analysis of XPS spectra of Fe²⁺ and Fe³⁺ ions in oxide materials. Appl. Surf. Sci. 254, 2441–2449.
 Yang, I., Edwards, K., 1984. Releases of radium and uranium into Ralston Creek and
- Yang, I., Edwards, K., 1984. Releases of radium and uranium into Raiston Creek and Reservoir Colorado, from uranium mining. In: Barney, G.S., Navratil, J.D., Schulz, W.V.V. (Eds.), Geochemical behavior of disposed radioactive waste. Symposium series, 246. American Chemical Society, Washington, DC, pp. 271–286.
- Yin, M., Sun, J., Chen, Y., Wang, J., Shang, J., Belshaw, N., Shen, C., Liu, J., Li, H., Linghu, W., Xiao, T., Dong, X., Song, G., Xiao, E., Chen, D., 2019. Mechanism of uranium release from uranium mill tailings under long-term exposure to simulated acid rain: geochemical evidence and environmental implication. Environ. Pollut. 244, 174–181.
- Yin, M., Tsang, D., Sun, J., Wang, J., Shang, J., Fang, F., Liu, J., Song, G., Xiao, T., Chen, D., 2020. Critical insight and indication on particle size effects towards uranium release from uranium mill tailings: Geochemical and mineralogical aspects. Chemosphere 250, 126315.
- Yin, M., Zhou, Y., Tsang, D., Beiyuan, J., Song, L., She, J., Wang, J., Zhu, L., Fang, F., Wang, L., Liu, J., Liu, Y., Song, G., Chen, D., Xiao, T., 2021. Emergent thallium exposure from uranium mill tailings. J. Hazard. Mater. 407, 124402.
- Yusoff, A.H., Mohamed, C., 2017. Accumulation of natural uranium isotopes in Malaysian harbour sediment. J. Oceanogr. Mar. Res. 5, 1–10.
- Yusoff, A.H., Sabuti, A.A., Mohamed, C.A., 2015. Natural uranium and thorium isotopes in sediment cores off Malaysian ports. Ocean Sci. J. 50, 403–412.