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Invited review

Uranium mobility in organic matter-rich sediments: A review of geological and geochemical processes

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ABSTRACT

Uranium (U) is of enormous global importance because of its use in energy generation, albeit with potential environmental legacies. While naturally occurring U is widespread in the Earth's crust at concentrations of ~1 to 3 ppm, higher concentrations can be found, including within organic matter (OM)-rich sediments, leading to economic extraction opportunities. The primary determinants of U behaviour in ore systems are pH, Eh, U oxidation state (U(IV), U(VI)) and the abundance of CO_3^{2-} ions. The concentration/availability and interrelationships among such determinants vary, and the solubility and mobility of ions (e.g. OH^-, CO_3^{2-}, PO_4^{3-}, SiO_4^{4-}, SO_4^{2-}) that compete for U (primarily as U(VI)) will also influence the mobility of U. In addition, the presence of OM can influence U mobility and fate by the degree of OM sorption to mineral surfaces (e.g. Fe- and Si- oxides and hydroxides). Within solid-phase OM, microbes can influence U oxidation state and U stability through direct enzymatic reduction, biosorption, biomineralisation and bioaccumulation. The biogenic UO_2 product is, however, reported to be readily susceptible to reoxidation and therefore more likely remobilised over longer time periods. Thus several areas of uncertainty remain with respect to factors contributing to U accumulation, stability and/or (re)mobilisation. To address these uncertainties, this paper reviews U dynamics at both geological and molecular scales.

Here we identify U-OM bond values that are in agreement, relatively strong, independent from ionic strength and which may facilitate either U mobilisation or immobilisation, depending on environmental conditions. We also examine knowledge gaps in the literature, with U-OM solubility data generally lacking in comparison to data for U sorption and dissolution, and little information available on multi-component relationships, such as U-OM-V (V as vanadate). Furthermore, the capability of OM to influence the oxidation state of U at near surface conditions remains unclear, as it can be postulated that electron shuttling by OM may contribute to changes in U redox state otherwise mediated by bacteria. Geochemical modelling of the environmental mobility of U will require incorporation of data from multi-corporation studies, as well as from studies of U-OM microbial interactions, all of which are considered in this review.

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1. Introduction

Naturally occurring uranium (U) ore deposits are important to society as a primary material for the generation of nuclear power (CoA, 2006; IAEA, 2009; OECD-NEA, 2012). With U-bearing ore resources being finite and widely dispersed, devising better strategies to locate and extract U from these ores remains an imperative (Bowell et al., 2011; Kreuzer et al., 2010). Uranium ore deposits have been identified within sandstone, breccia, organic matter (OM)-rich sediments, unconformities, roll-front formations and granitic plutons across all continents (Bali, 2012; Bowie, 1979; Cuney, 2009; Cuney, 2010; Mills et al., 2008). This review will discuss the presence of U within OM-rich sedimentary deposits. As research and exploration are directed towards a wider array of geological settings, increasingly OM-rich deposits will be considered because of their potential richness in U and other elements (Breger, 1974; Dickson and Giblin, 2007; Disnar and Sureau, 1990; Douglas et al., 2011; Gize, 2000; Greenwood et al., 2013; Idiz et al., 1986; Jaraula et al., 2015; Landais, 1993; Landais, 1996; Landais et al., 1987; Leventhal et al., 1986; Leventhal et al., 1987; Lewan and Buchardt, 1989; Pirlo and Giblin, 2004; Rose and Wright, 1980). Indeed, the economic viability of mining activity may be enhanced through co-product mining as illustrated by U and vanadium (V) extraction in the Colorado Plateau region of the United States (US) (Shawe, 2011). Whereas the importance of considering U within OM-rich sedimentary deposits is recognised, the relative stability and mobility of resident U is still poorly understood (Sandino and Bruno, 1992; Yang et al., 2012).

Two primary reasons can be proposed for why U mobility within OM-rich deposits remains uncertain. First, OM-rich deposits are heterogeneous in their composition, complex in the way that these heterogeneous components interact, and diverse in their macro-geological setting. For example, individual deposits can include a diverse range of ions, elements and microbes, which can interact within settings characterised by differing Eh-pH environments and geological formation (e.g. roll front deposits). Second, OM-rich deposits have historically been difficult to analyse due to technological limitations. As new analytical and characterisation techniques have emerged, deeper insights have been obtained into deposit heterogeneity, which better elucidate constituent relationships. What remains missing is a synthesis of relevant field and laboratory-based investigations to reach conclusions about the breadth and significance of multi-component relationships involving U. Such relationships involve the interactions among U, OM and other elements or complexes that can have implications for crustal U mobility and cycling (Cuney, 2010).

Physical and chemical factors shaping U stability and mobility have changed over geologic time. Environmental processes such as mechanical and chemical rock weathering release U and enable it to be cycled through both particulate/mineral and dissolved forms from sources to sinks over geological time scales. The incorporation or release of U to or from mineral structures is determined primarily by its oxidation state and mineral solubility (Maher et al., 2012). In its +4 oxidation state (U(IV)), U is less soluble and forms more stable compounds than in its +6 oxidation state (U(VI)), which is more readily mobilised. There are many factors that determine the oxidation/reduction of U from inorganic physicochemical (e.g. pH, Eh, pO_2, pCO_2) to organic and microbial enzymatic mechanisms (Campbell et al., 2012; Law et al., 2011; Newsome et al., 2014). Following the Great Oxidation Event (GOE), the increased availability of reactive oxygen intensified parent rock weathering, enabled oxidation of low solubility U(IV) minerals, and expanded the number of more mobile U(VI) species. Stemming from the accumulation of plant debris and the aqueous mobility of secondary U, ancient and recent geological U deposits exist in organic-rich sedimentary layers at concentrations up to hundreds of ppm. The geochemical factors affecting U stability and mobility within these organic-rich sediments are inherently complex, and this complexity is amplified by the diversity of organic matter (OM) origins and types.

The mobility of U is also influenced by the type and the strength of bonding to available ligands. Whereas U(IV) bonds are covalent with oxygen and silica (via oxygen), with the product generally sparingly soluble, U(VI) complexes are numerous and can involve a range of ligands (Burns, 2005; Burns et al., 1997). The latter are centred upon the uranyl cation (UO_2^{2+}) which allows formation of a range of anionic complexes, such as the tricarbonate uranyl anion ($UO_2(CO_3)_3^{4-}$)), that vary in solubility and mobility. These uranyl-anionic complexes are widely reported, but how they interact with OM, mineral surfaces and/or with microbial cells remains less well understood. To understand the fate of U therefore requires consideration and modelling of multi-component relationships. In this review, we integrate existing research on factors influencing the relative stability and mobility of U within low temperature environments, with specific attention to OM-rich sedimentary deposits.

To address the above themes, this review is divided into three sections. The first section explores geological processes shaping the formation and remobilisation of U deposits, including rock weathering, the evolution of the Earth's atmosphere and roll front deposits where OM-rich environments are recognised as potential U 'sinks'. The second section then presents a comprehensive review of the stability and mobility of U - by considering the oxidation state of U, the solubility of U compounds and the sorption of U species. Two sub-sections specifically focus on the influence of Fe oxides on U sorption and the influence of OM on U speciation within sedimentary deposits. A final section then considers multi-component systems, including U, OM and other constituents, and their incorporation into surface complexation models (SCM) and reactive transport models (RTM).

2. Uranium stability and mobility at geological scales

Previous research has revealed high concentrations of U within low temperature sedimentary rocks (>20% at Oklo, Gabon (Gauthier-Lafaye et al., 1989)) and OM-rich sedimentary deposits (averaging 12–84 ppm U) (Cuney, 2010). These findings have particular importance considering that such U concentrations are significantly higher in these materials than in the parent igneous rocks. Throughout the Earth's crust U occurs at concentrations of approximately 1 to 3 ppm (Fayek et al., 2011; Hazen et al., 2009). Basalts average around 1 ppm U (Alloway, 2013), whilst more felsic igneous rocks are relatively enriched, with about 3.6 ppm and 5.0 ppm in granites and rhyolites, respectively (Hobday and Galloway, 1999). Some granites may contain greater than 8 ppm U (Alloway, 2013), including up to 50 ppm within Proterozoic units in the Musgrave region of Western Australia, (Kreuzer et al., 2010) which is the assumed parent rock for U in nearby sedimentary deposits (Hobday and Galloway, 1999).

In contrast, sedimentary rocks, including black shales, breccias, clays, limestones, phosphorites and sandstones, may contain an average of 4 ppm U (Alloway, 2013). Notable examples of high concentrations include the Olympic Dam breccia deposit (Australia), where U is present at approximately 300 ppm (as U_3O_8 resource of 1474 Mt. at U grade of 0.027% U_3O_8) (Kreuzer et al., 2010; Pownceby and Johnson, 2014). Low U concentrations of 2–4 ppm are typically found in black shales (Spirakis, 1996), with much higher concentrations of up to 700 ppm U identified in phosphorite-black shale deposits (Bowell et al., 2011). In addition to sedimentary rocks, U has been found in both recent and ancient OM-rich sediments (Bowell et al., 2011; Dosseto et al., 2006; Douglas et al., 2011; Meunier et al., 1989; Owen and Otton, 1995). Examples include peat, lignites, coals, oils and black shales (Dill, 1987; Ellsworth, 1928b; Gentry et al., 1976; Langmuir, 1978; Mossman, 1999; Zielinski and Meier, 1988). Variations in U concentration exist across these types of OM deposits, with some of the most highly enriched being diagenetically altered lignites (Leventhal et al., 1986; Szalay, 1964). Examples include the North and South Dakota lignites (US) and the tertiary lignites of the Ebro Valley (Spain), reported to contain as much as 500–2500 ppm U as U_30_8 (Bowie, 1979; Douglas et al., 2011).

To understand why U can be highly concentrated within sedimentary environments, it is useful to consider first the stability and mobility of U over geological spatial and temporal scales. Various reviews provide insight into the crustal mobility of U, some focusing on periods of planetary evolution and others considering the potential for biogeochemical cycles within these periods. Cuney (2010) categorises the "evolution" of U species on Earth into four main time periods: (1) mantle melting to ~3.2 Ga; (2) mantle cooling and the crystallisation of U in granites between ~3.2 to ~2.2 Ga; (3) oxygenation of the atmosphere at ~2.2 Ga, facilitating the widespread oxidation of U(IV) to the soluble and more mobile U(VI), and increasing the diversity of U-bearing minerals; and (4) angiosperm plants during the Cretaceous period leading to increased availability of phosphate, which has uranophilic characteristics. Over 400 U deposits are estimated to have been formed globally during this fourth period, many in sandstones (Cuney, 2010), with some included in layers that are OM-rich.

Additional stages to the aforementioned periods have been identified. For example, Hazen et al. (2009) acknowledges tectonic processes and anaerobic processes occurring or evolving between periods (2) and (3) stated above. Through tectonic processes, including subduction and volcanic activity, diverse igneous (i.e., mainly granitic in the case of U) rocks are cycled to the Earth's surface where weathering subsequently releases U, thus enabling U transportation and deposition. Over time, sediments containing U are buried and metamorphosed through high T-P conditions deep within the Earth's crust, with subsequent tectonic activity allowing U to recycle to the Earth's surface. Thus, U can also be found at significant concentrations in metamorphic rocks and within weathering and chemically resistant phases such as zircons (Davis et al., 2003; Maas et al., 1992; Rose and Wright, 1980).

The above conceptualisation of the geological cycling of U is further complicated by other geophysical processes, including faulting and folding, uplift, mass erosion (e.g., landslides) and subduction (Fyfe and Brown, 1979). A geochemical dynamic, to which Cuney (2010) alludes, was the period of relatively rapid increase in atmospheric oxygen known as the Great Oxidation Event (GOE). The GOE constituted a critical geochemical threshold in Earth's evolution because increased atmospheric oxygen intensified weathering and greatly enhanced the remobilisation of U (Och and Shields-Zhou, 2012). A second key change stimulated by the GOE was an increased rate of eukaryotic evolution in the oxygenated environment, thus expanding biomass and the production of OM-rich sediments capable of enrichment in U (Dill, 2010; Kelepertsis, 1981). Thirdly, due to rising oxygen concentrations, cyclic chemical reactions involving oxidation-reduction (redox) were increasingly prevalent. The above factors brought about by the GOE had a strong influence on U geochemistry allowing continual cycling between +6 and +4 oxidation states – of which some products could be precipitated (Borch et al., 2010). These three points are briefly reviewed below.

2.1. Weathering and the GOE: implications for U cycling

Weathering constitutes a fundamental natural process through which U is released from its primary (e.g. granitic) or secondary (e.g. sedimentary) host rock. Rock is broken down into its principle components either mechanically or chemically, with the key agents being water, air and/or various geochemical species. Chemical weathering of parental rocks may also be facilitated microbially, both in the production of corrosive organic acids through detrital decomposition or direct enzyme action (Drever and Stillings, 1997; Graham, 1941; Lawrence et al., 2014; Matlakowska and Sklodowska, 2011; Oliva et al., 1999; Sparks, 1971). Whilst processes of weathering are well known, U (re)mobilisation within sedimentary systems, which would determine the nature of (secondary) U-(re)mineralisation has received less attention and may hold importance in ore-genesis (Granet et al., 2007; Idiz et al., 1986).

The type (e.g. chemical or mechanical) and intensity of weathering processes have varied over geological time. Prior to the GOE, approximately two billion years ago, chemical weathering was minimal due to low concentrations of oxygen in the atmosphere. Mechanical deformation induced by major tectonic events represented the dominant weathering pathway. Released materials were subsequently eroded to form quartz-pebble conglomerate deposits where U became trapped (e.g. Witwatersrand (SA) and Elliot Lake (USA) (Keegan et al., 2012)). Even where U was released from host/sedimentary rock, its degree of mobility was limited as prevailing freeze-thaw conditions produced larger less mobile fragments and low oxygen conditions maintained U in reduced oxidation states. During the Archean and earliest Proterozoic, U-bearing minerals lacked complexity and diversity and were probably restricted to insoluble U(IV) compounds, including uraninite (UO_2), and coffinite ($USiO_4$). Thus, because of U(IV) insolubility, U was relatively immobile. Only once these quartz-pebble conglomerate deposits

became re-exposed under the new O_2-enriched atmosphere, a second weathering process involving oxygen could then re-mobilise U as soluble U(VI) (Hazen et al., 2009; Robertson et al., 1978). Therefore accumulation of OM in sedimentary environments was limited, as evidenced by the absence of U within black shales older than 2.2 Ga (Cuney, 2010). Nevertheless, Tice and Lowe (2006) suggest that Archean U mobility was possible under anoxic conditions, postulating (from rare earth element - REE data) that solubilisation of U^{6+} by aqueous carbonate species (where Archean atmospheric pCO_2 was greater than today) would have been the main mechanism.

The GOE is associated with an evolutionary proliferation of photosynthetic bacteria, resulting in oxidation of an initially anoxic atmosphere (Hazen et al., 2009; Kump et al., 2011). The greater availability of oxygen induced various events, including the chemical weathering of igneous granitic rocks or tuffaceous parent rocks giving rise to new U deposit classes (Castor and Henry, 2000; Kovačević et al., 2009). Both on the surfaces as well as within such source rocks, tetravalent U was oxidised into U(VI), with the latter able to form an extended range of mineral types (Robertson et al., 1978). With the increased availability of oxygen in the atmosphere and upper crust, the number and complexity of U-bearing minerals increased to ~200 (Hazen et al., 2009). In addition to oxygenation from the surface atmosphere, U could be oxidised and then mobilised following contact with oxygenated groundwater and thus transported through porous strata. Once mobilised, soluble-U compounds could then redistribute and precipitate either as insoluble U(VI) compounds or reduced to U(IV) compounds leading to the formation of ore bodies. The GOE has also been linked to the proliferation of many other types of oxygen-containing minerals, including the Fe-oxides (Robertson et al., 1978) and sulphates, such as $CaSO_4$ (Hazen et al., 2009).

Within this context of crustal evolution, a number of studies have examined the extent to which solubilised U compounds are mobile (Hobday and Galloway, 1999; Murakami et al., 1997; Walton et al., 1981). Focusing on the sub-tropical Koongarra district in Northern Australia, Yanase et al. (1995) estimated that U migrated only 200 m from sources over timescales of 1–1.5 million years. Reasons for this limited migration were identified as including seasonal rainfall coupled with high evaporation rates, upper boundary constrictions represented by clay pans and constraints on the mobility of U in carbonate complexes by the presence of precipitate-forming phosphate and silicate species in high concentrations. That different geological constituents can retard the transportation of U has also been reported elsewhere (e.g. see Noubactep et al., 2006 on the influence of silicates and pyrites).

Whilst the local and regional hydrology has importance in retaining the developing ore body (Robertson et al., 1978), the redox status must be considered as it generally determines the solubility and therefore potential flux of constituents (Ragnarsdottir and Charlet, 2000). Robertson et al. (1978) suggests that where high U concentrations are found in porous sandstones is indicative of a closed system. Closed systems can contain clay-rich impermeable layers, such as siltstones (Dequincey et al., 2002; Seredin and Finkelman, 2008), which limit solute movement and thus form barriers from the closely-packed nature of the grains preventing the movement of U and other elements. Alternatively a system may be closed because of the absence of groundwater, which Robertson et al. (1978) contrasts with open freely-draining systems that are reported to be low in minable U. The implication of system hydrology is that in the absence of retarding factors (e.g. sorption), U as solutes may transition over considerable distances, often aided by preferential fracture-flow (Jardine et al., 2002; Luo and Gu, 2008; Robertson et al., 1978).

2.2. Genesis of organic-rich deposits after the GOE

Cuney (2010) states that with the commencement of the GOE, the next major episode in the history of U mineral deposition involved the proliferation of eukaryotic growth. With algal and plant growth also came the deposition of OM. Through humification, OM was broken down into humus (Wershaw, 1994). Humification is a continuing process that involves many fungal and microbial dimensions, including direct enzymatic reactions which break down highly structured hemi-celluloses and lignins into simpler plant sugars and acids (Meyers and Ishiwatari, 1993; Szalay, 1964; Wershaw, 1994). The rate of humification is related to the microbial response to temperature and climatic conditions at the time of deposition (Zhong et al., 2010). Following the initiation of the GOE the rate of humification intensified, weathered and mobile U increasingly became trapped within accumulating layers of detritus and humus, eventually forming U-deposits (Drennan and Robb, 2006; Szalay, 1964). As described by Szalay (1964), the geochemical enrichment of U in peats can be as high as 10,000 times over the co-existing solute, which he attributed to the high cation exchange capacity of the constituent humic acids. Rather than static layers, early microbial activity may have allowed localised migration of constituent material. More substantive redistribution, as well as the entry of new material, was likely through groundwater infiltration. Through this infiltration, further additions of U were possible into the layers of OM-rich sediments.

As summarised in Table 1, various case studies have highlighted the presence of U within OM-rich sediments, describing the type of organics, the minerals present and U concentrations. A common theme across these studied deposits is that U occurs both as uraninite and coffinite, and is often present alongside a heterogeneous mix of heavier elements, including the REEs. Additional research has provided evidence suggesting that the U(IV) minerals present are in fact alteration products of previously mobilised U(VI), as seen accumulated within OM and on the rims of other U-minerals (Deditius et al., 2008; Zielinski and Meier, 1988). Complex U-OM associations have also been long acknowledged, such as thucholite (a mix of hydrocarbons, uraninite and sulphides), identified by Ellsworth (Ellsworth, 1928a; Ellsworth, 1928b). As a consequence of the GOE and the growth of detritus was the expanded availability of phosphate within OM-sediments. As Cuney (2010) acknowledges, this promoted a range of new U(VI)-PO_4 compounds, for example, metatorbernite [$Cu(UO_2)_2(PO_4)_2 \cdot 8H_2O$], autunite [$Ca(UO_2)_2(PO_4)_2.10$–$12H_2O$] or saléeite [$Mg(UO_2)_2(PO_4)_2 \cdot 10H_2O$] (see Table 2). Following the early accumulation of U within OM-rich sediments, three longer term influences play a crucial role in the stabilisation of U to form deposits. These influences which are discussed below are microbial activity, radiolysis and diagenesis. Whilst potentially occurring simultaneously, the effects of radiolysis and diagenesis are likely to be more relevant over longer timeframes.

2.2.1. Microbial processes affecting U redox state in organic matter

Organic detritus (e.g. humus) undergoes important structural changes during the earliest stages of deposition through microbial decomposition (Stewart et al., 2011). As larger molecules are broken down to lower molecular weight moieties, then electron shuttling may occur between these molecules and microbes (Newsome et al., 2014; Roden et al., 2010). Another consequence of this microbial activity within the OM is the creation of reducing conditions, particularly once oxygen becomes limited (Wan et al., 2008). Redox-sensitive metals, which include Fe, Mn and U, provide a terminal acceptor for electrons for more specialised microorganisms when other available electron acceptors have become limited (e.g. NO_3^-, SO_4^{2-}). Depending on the microbe type, such metals may either be the principle or secondary acceptor of electrons (Sitte et al., 2010). For example, in the case of sulphate-reducing bacteria (SRB), the bacteria may switch to reducing U^{6+} after sulphate has become exhausted (Anderson et al., 2011). Microbially-driven U-reduction is the focus of an expanding body of research (Fomina et al., 2007; Gadd and Fomina, 2011; Liger et al., 1999; Lovley et al., 1991; Min et al., 2005; Regenspurg et al., 2010) and reviews (Anderson et al., 2011; Campbell et al., 2014; Newsome et al., 2014; Wilkins et al., 2006). Whilst the focus of this research is largely related to mining and nuclear site remediation, parallels can be drawn in U deposit formation in OM sediments (Law et al., 2011). In particular, several mechanisms are commonly identified through which U is processed

Table 1
Characteristics of some organic-rich sedimentary deposits hosting uranium.

Deposit and location	Age	Concentration/yield	U-minerals present	Other minerals	Composition of hosting material	Reference
Kern Country, California, US	Recent, surficial	Bedrock: 3.7–7.1 ppm U Fresh bog U ppm, not specified	Not specified	Enriched in: V, Fe and Mo Minerals not specified	Bedrock: quartz diorite Bog sediment: 4.5% TOC living plants U ppm source: calcareous sandstone	[1]
Caithness, Scotland, UK	4000 yrs	0.1% U	U-*Si*-Ti phases			[2]
South Texas, US	Host rock -upper Eocene (20–30 Ma) Source rock - Miocene (~20 Ma)	4.38% U	Coffinite Other phases not identified		Lignite-sandstone Roll-front type deposit Catahoula Tuff identified as source rock	[3,4]
Mulga Rock, Western Australia, Au	Middle Eocene (30–50 Ma)	0.03–8.2% U 13,000 U tonnes	Coffinite, brannerite	Diverse mineral assemblage: REE, galena, pyrite, sphalerite, barite, rutile, anatase, zircon, ilmenite, cassiterite, monazite, xenotime	Lignite host capped with clay and sand. Overlies Precambrian basement with tertiary sedimentary sandstone	[5,6]
The Coutras Deposit, Gironde, France	Middle Eocene (30–50 Ma)	0.1% U/20,000 tons U	Coffinite needles	V, Se, pyrite, kaolinite	Arenaceous, Tabular Not diagenetic	[7,8]
Claude Deposit, Cluff Lake, Canada	Middle Eocene (30–50 Ma)	0.5% U/10^6 tons ore/5000 tons U	85% uraninite, minor coffinite	Galena, pyrite, geroffinite ((Ni, Co, Fe) As S) altaite (PBTe), chalcopyrite, clausthalite, molybdenite, jodisite, mavite, gold, sphalarite, selenides	Blebs and pods of OM associated with U min OM black, brittle with sub vitreous lustre	[9]
Henry Mountains Morrison Formation, Colorado Plateau, US	U-Pb ages Minimum age of 115 Ma	Not specified	Coffinite (2–6 μm) Dolomite –coffinite, Minor pitchblende	V-bearing chlorite, V-oxides, dolomite, pyrite	Unoxidised tabular U–V—ore Detrital OM Calcite in sandstone not located with U ore	[10]
Slick Rock Colorado Morrison Formation, Plateau, US	132–115 Ma	Not specified	Tabular— U-V ore, coffinite, uraninite, montroseite	Fine grained V-silicates, pyrite, authigenic calcite, dolomite, barite, hematite and kaolinite in sandstones	Coalified detrital OM present in and around ores Strongly corroded quartz and feldspar	[10]
Grants Uranium Region, Morrison Formation, Colorado Plateau, US	132 Ma (U–Pb ages)	Not specified	Course-grained coffinite (<2 μm)	Authigenic vanadium chlorite, V-oxides, smegtite, pyrite, calcite, etched garnets	Early diagenesis Amorphous aromatic OM from humic acids Iron leached from Fe–Ti oxides Chlorite overgrowths in amorphous OM smectite grain coatings	[10]
Francevillian, Gabon, West Africa	2000 Ma	2–10 ppm U 1.45% U with Mineralised bitumen	Unidentified, Amorphous or finely dispersed uraninite, Coffinite		OM of High thermal maturity With bitumen, oils and black shales	[11]
Old Rifle site ,US	Recent	U concentrations in the groundwater are between 0.1 and 0.4 U ppm, as U(VI)-carbonate and Ca–U(VI)-carbonate ternary species.	Not specified	Dominated by quartz and feldspar (both plagioclase and alkali-feldspar), with lesser amounts of amphiboles and clay. Clays: clinochlore, illite and smectite Fe Oxides- hematite, magnetite and goethite	Modern natural and contaminated aquifer The aquifer sediment is primarily an alluvial deposit from the nearby Colorado River, containing unconsolidated clay, silt sand, gravel and cobbles	[12,13]

References: [1] (Idiz et al., 1986); [2] (Read et al., 1993); [3] (Ilger et al., 1987); [4] (Reynolds et al., 1982); [5] (Douglas et al., 2011); [6] (Douglas et al., 1993); [7] (Meunier et al., 1992); [8] (Meunier et al., 1989); [9] (Leventhal et al., 1987); [10] (Hansley and Spirakis, 1992); [11] (Cortial et al., 1990); [12] (Campbell et al., 2012); [13] (Qafoku et al., 2009).

biotically: biosorption; direct enzymatic reduction; bio-mineralisation; and bioaccumulation. These mechanisms are now examined.

Biosorption involves the passive, often rapid, uptake of ions and particles, including U, onto living or dead biological matter (Ozaki et al., 2005; Tsezos and Volesky, 1982). Biosorption occurs because the electrical surface charges (as a function of pH and ionic strength) provided by bacterial or fungal biomass attract oppositely charged ions, such as UO_2^{2+}. The efficiency of this process depends on the strength of binding to the carboxyl, amine, hydroxyl, phosphate or sulfhydryl ligands present in cell walls (Newsome et al., 2014). Microbial waste products (e.g. extracellular polysaccharides, EPS) are also able to attract positively charged metal ions or species (Anderson et al., 2011). Siderophores, which are metal-specific ligands produced by microbes, are designed to capture metal ions at low concentrations (Anderson et al., 2011; Escher and Sigg, 2004; Kalinowski et al., 2004). Siderophores and the pyoverdin subgroups are recognised to be important in U biosorption because of their strong affinity for radionuclides (Anderson et al., 2011; Behrends et al., 2012; Kalinowski et al., 2004).

Table 2
Uranium compounds and mineral names, formulas and alternative formulas (the oxidation state is U(VI) unless otherwise stated).

Mineral name	Formula	Reference
Carbonates		
Andersonite	$(Na_2K_3^-UO_3(CO_3)_3(H_2O)_6)$	[1], [2]
Bayleyite	$(Mg_2UO_2(CO_3)_3(H_2O)_{18})$	[1], [2]
Grimselite	$(NaK_3UO_2^-(CO_3)3H_2O)$	[1], [2]
Liebigite	$(Ca_2UO_2(CO_3)_3(H_2O)_{10})$	[1]
Rutherfordine	UO_2CO_3	[1],[3]
Swartzite	$CaMgUO_2(CO_3)_3(H_2O)_{12}$	[1], [2]
Schrockingerite	$NaCa_3UO_2(CO_3)_3SO_4F(H_2O)_{10}$	[1], [2]
Wyartite (U(V))	$CaU^{5+}(UO_2)_2(CO_3)O_4(OH)(H_2O)_7$	[4]
Oxide		
Metaschoepite	$UO_3(H_2O)_2$	[5]
Metastudtite	$UO_4(H_2O)_2$	[1]
Pitchblende	U_3O_8 $U_2O_5 \cdot UO_3$	[6]
Schoepite	$(UO_2)_8O_2(OH)_{12} \cdot 12H_2O$	[3], [5], [7]
Studtite	$UO_2O_2(H_2O)_4$	[1], [8], [9]
Uraninite (U(IV))	UO_2	
Phosphates		
Autunite	$Ca(UO_2)_2(PO_4)_2$ $Ca(UO_2)_2(PO_4)_2 \cdot 8\text{-}12H_2O$	[10], [11], [12]
Bassetite	$Fe((UO_2)(PO_4))_2(H_2O)_8$	[13]
Chernikovite	$H_3O(U_2O)PO_4(H_2O)_3$	[1]
Meta-ankoleite	$KUO_2PO_4(H_2O)_4$	[1]
Meta-autunite	$[Ca(UO_2)_2(PO_4)_2(H_2O)_6]$	[8], [11], [12], [13], [14]
Meta-torbernite	$[Cu(UO_2)_2(PO_4)_2 \cdot 8H_2O]$	[11]
Phosphuranylite-groups	$KCa(H_3O)_3(UO_2)_7(PO_4)_4O_4 \cdot 8(H_2O)$	
Saleeite	$[Mg(UO_2)_2(PO_4)_2 \cdot 10H_2O]$	[17]
Torbernite	$Cu[(UO_2)(PO_4)]_2 \cdot 10\text{–}12H_2O$	[8], [11], [14], [15], [16], [17]
Rare Earth elements		
Betafite	$(Ca,U)_2(Nb,Ti)_2O_6OH$	[18]
Brannerite	$(U, Ca, Y, Ce, La)(Ti, Fe)_2\ O_6$	[18], [20]
Davidite	$(La, Ce)(Y,U,Fe)(Ti,Fe)_{20}(O,OH)_{38}$	[18]
Kasolite	$(Pb(UO_2)(SiO_4)H_2O)$	[1]
Silicates		
Coffinite (U(IV))	$USiO_4$	[13], [22], [23], [24], [25]
Slodowskite	$Mg[(UO_2)(SiO_3OH)]_2\text{-}(H_2O)_6$	[1]
Boltwoodite	$(Na,K)(UO_2)(HSiO_4) \cdot H_2O$	[1], [8],[19], [26]
Haiweeite	$(Ca(UO_2)_2(Si_2O_5)_3(H_2O)_5)$	[1]
Soddyite	$(UO_2)SiO_4(H_2O)_2$ $(UO_2)_2(SiO_4)\ (H_2O)_2$	[1],[19]
Swamboite	$U^{6+}\ (UO_2)_6(SiO_3OH)_6(H_2O)_{30}$	[25]
Uranophane	$Ca(UO_2)_2\ Si_2O_7 \cdot 6H_2O$ $Ca_2(UO_2)_2(SiO_3OH)_2$ $Ca(UO_2)_2\ (SiO_3)(OH)_2 \cdot 5H_2O$ $Ca(H_3O)_2(UO_2)(SiO_4)_2(H_2O)_3$ $Ca(UO_2)_2(HSiO_4)_2 \cdot 5H_2O$	[1].[3],[6],[18],[19], [21]
Sulphates		
Deliensite	$Fe(UO_2)_2(SO_4)_2(OH)_2(H_2O)_3$	[13]
Johannite	$Cu(UO_2)^{2-}\ (SO_4)_2\ (OH)_2 \cdot H_2O_8$	[25]
Uranopilite	$(UO_2)_6(SO_4)O_2(OH)_6(H2O)_6 \cdot 8H_2O$	[25]
Zippeite	Mg, Co, Ni, Zn, Na, K, $NH_4\ (UO_2)_6\ (SO_4)_3(OH)_{10}(H_2O)_x$	[1], [27], [28]
Vanadates		
Carnotite	$K2(UO_2)_2(VO_4)_2$ $K(UO_2)_2(VO_4)_2 \cdot 13H_2O$ $K_2(UO_2)(V_2O_8) \cdot 3H_2O$	[3], [20], [29], [30], [31]
Curienite	$Pb_2(UO_2)(V_2O_8) \cdot 5H_2O$	[30]
Francevillite	$Ba,Pb(UO_2)(V_2O_8) \cdot 5H_2O$	[30]
Metatyuyamunite	$Ca(UO_2)(V_2O_8) \cdot 3H_2O$	[30]
Strelkinite	$Na_2(UO_2)(V_2O_8) \cdot 6H_2O$	[30]
Tyuyamunite	$Ca(UO_2)_2(VO_4)_2 \cdot 5\text{-}8H_2O$ $Ca(UO_2)(V_2O_8) \cdot 9H_2O$	[3], [6], [18], [30], [31], [32]
Vanuralite	$Al(OH)(UO_2)_2(V_2O_8) \cdot 3H_2O$	[30]

[1] (Gorman-Lewis et al., 2008a); [2] (O'Brien and Williams, 1983); [3] (Langmuir, 1978); [4] (Burns and Finch 1999) [5] (Gorman-Lewis et al., 2008b); [6] (Alloway, 2013); [7] (Elless and Lee, 1998); [8] (Burns, 2005); [9] (Burns, 2011); [10] (Ray et al., 2011); [11] (Locock and Burns, 2003); [12] (Gorman-Lewis et al., 2009); [13] (Deditius et al., 2008); [14] (Burns, 1999); [15] (Burns et al., 1997); [16] (Wylie et al., 2012); [17] (Murakami et al., 1997); [18] (Bowell et al., 2011); [19] (Shvareva et al., 2011); [20] (Fayek et al., 2011); [21] (Jouffret et al., 2010) [22] (Özkendir, 2010); [23] (Pointeau et al., 2009); [24] (Dreissig et al., 2011); [25] (Gorman-Lewis et al., 2007); [26] (Burns, 2001); [27](Brugger et al., 2003); [28] (O'Brien and Williams, 1981); [29] (Locock et al., 2004);.[30] (Frost et al., 2005);[31] (Tokunaga et al., 2009); [32] (Tokunaga et al., 2012).

Microbial extracellular material may also be involved in U immobilisation through direct or indirect enzymatic reduction of U(VI) to U(IV) (Ginder-Vogel and Fendorf, 2007; Lovley and Phillips, 1992; Lovley et al., 1991; Lovley et al., 1993; Suzuki et al., 2003). In recent studies, direct enzymatic reduction has been demonstrated to be effective at U(VI) reduction and may dominate under ambient conditions (Bargar et al., 2013; Newsome et al., 2014). The control of U migration in contaminated sediments through direct enzymatic reduction using microbes has received substantial attention (Bargar et al., 2013; Suzuki et al., 2005). Equally such mechanisms could have relevance for U deposition, particularly where OM is abundant (Lovley and Coates, 1997), as the rate of U(VI) reduction has been linked to the presence of OM. Experiments

have shown that, with the addition of ethanol and/or acetate, U(VI) microbial reduction rates were increased (Alessi et al., 2014a; Bargar et al., 2013; Finneran et al., 2002; Williams et al., 2011).

Following sorption and reduction processes, "biomineralisation" can occur. Biomineralisation describes the process of metal and inorganic ligand precipitation at the cell surface to form poorly-crystalline or crystalline structures. Observations of U bio-minerals in nature are rarely reported, with a few cases found in coals (Min et al., 2005). There have, however, been a number of laboratory-based studies that have investigated this process in detail (Suzuki et al., 2005). Such studies have mainly focussed on the influence of U biomineraliation with and without OM (humic acids), Fe-oxides, PO_4^{3-}, CO_3^{2-} and Ca^{2+} ions. Uncertainties exist in relation to the stability and longevity of biogenically-reduced U, especially under oxidising conditions (Newsome et al., 2014). Biogenically-reduced U is not coordinated in the same way as uraninite. Labelled as "non-uraninite" by some authors (Bernier-Latmani et al., 2010; Latta et al., 2012; Sharp et al., 2011), it is described as being poorly structured and monomeric (Bargar et al., 2013; Cerrato et al., 2013). This type of material may be unstable and could be readily oxidised over time compared to uraninite because of a higher number of reactive surface sites (Alessi et al., 2014a; Cerrato et al., 2013; Wan et al., 2005; Wan et al., 2008).

Mechanisms that involve active cell uptake of essential elements may also permit "bioaccumulation" of metals because of apparent molecular and/or stereochemical similarities. Bioaccumulation differs from biosorption in that it is metabolically dependant (Fomina et al., 2007). In the case of U, there is no known nutritional benefit to the cell, and U can in fact be harmful or toxic (Acharya and Apte, 2013). The bioaccumulation of U within cells may also occur through the passive forms of uptake caused by the detrimental impact of U on cell membranes, thus enhancing cell permeability. Whether active or passive, to our knowledge, bioaccumulation of U in bacteria has only been observed in the laboratory (Newsome et al., 2014). Bioaccumulation has been observed in algae, but only at low pH and low carbonate alkalinity (<10 mmol L^{-1}) (Duff et al., 1997). Other organisms, such as yeasts, filamentous fungi and lichens, are also able to bioaccumulate U, as autunite, ranging from 10 to 280 mg g^{-1} of dried biomass (Fomina et al., 2007; Gadd and Fomina, 2011).

Building on the processes introduced above, through which U is processed biotically, various studies can be identified that have recognised chemical species including PO_4^{3-}, CO_3^{2-} and Ca^{2+} that may enhance or retard the intensity of microbial U processing. Where phosphates are available, the enhanced biomineralisation of U-phosphates is reported (Newsome et al., 2014; Salome et al., 2013). Microorganisms commonly produce the enzyme phosphatase, which under a broad range of conditions catalyses the transformation of organically-bound phosphate to inorganic phosphate (Beazley et al., 2011; Salome et al., 2013). During this transformation, available U may bond with phosphate forming uranyl phosphates, especially under low pH. Uranyl phosphate production has been observed with *Citrobacter sp.* (Macaskie et al., 1992) and with *Shewanella oneidensis* (Alessi et al., 2014b) by enzymatically mediated growth with end products obtained such as autunite or meta autunite (Fomina et al., 2007; Ray et al., 2011). Phosphatase activity has been applied to remediate contaminated sites, and has been demonstrated to remove U under a range of aerobic and anaerobic conditions at low to neutral pH (Beazley et al., 2011).

In contrast, carbonates have been found to significantly retard the rate of microbial U reduction (Ulrich et al., 2011). This is likely due to the strong affinity of U to carbonates, and the formation of uranyl carbonates; the latter greatly increasing U mobility at circumneutral pH (Behrends and Van Cappellen, 2005; Cheng et al., 2012). In a study by Behrends and Van Cappellen (2005), it was shown that direct enzymatic reduction by *Shewanella putrefaciens* in the presence of Fe(II) was inhibited by additions of $NaHCO_3$ which was attributed to preferential complexation. Like carbonates, the presence of Ca^{2+} is thought likely to retard bioprocessing of U. Counter-ions like Ca^{2+} are reported to interfere with the above-mentioned biosorption process, even promoting desorption (Brooks et al., 2003). Ulrich et al. (2011) has also shown that U(VI) bioreduction processes (by *Shewanella oneidensis*) was significantly retarded with increasing concentration of Ca^{2+}. In addition, Ca^{2+} may impede biomineralisation due to competition with other ions, and cause alteration of cell wall properties (Plette et al., 1996). The influence of Ca^{2+} may, however, be counteracted by the presence of other constituents. For example, both goethite and hematite can decrease the solution concentration of dissolved Ca^{2+} through adsorption, thus diminishing its negative effect on U(VI) reduction (Lloyd and Gadd, 2011; Stewart et al., 2011).

One commonality across many of the laboratory studies introduced above is the tendency to focus on individual bacterial or fungal strains in U(VI) reduction. In the natural world, microbes occur within localised functional ecosystems characterised by their microbial diversity (Istok et al., 2010; Mondani et al., 2011). Within such ecosystems, competition as well as complex synergies may exist between distinct microbial groups, and shifts in the balance of microbial populations can occur with changes in trophic conditions. For example, research has pointed to the possibility of sulphate-reducing bacteria out-competing Fe-reducing bacteria for added acetate, at which point U(VI) reduction slowed or ceased (Anderson et al., 2003; Istok et al., 2010). In view of this complexity, further examination of the role of microbial functional groups, both individually and interactively, in U reduction and mineralisation is warranted (Behrends and Van Cappellen, 2005; Wilkins et al., 2006).

2.2.2. Influence of radiogenic activities in OM

The second longer-term influence on the evolution of U-OM deposits introduced above was radiolysis. Natural decay from radionuclides can manifest in the form of radiolytic damage to OM. This phenomenon results in the structural breakdown of OM, where there is the localised cleavage of OM-OH bonds and damage to OM-functional groups (Drennan and Robb, 2006; Gentry et al., 1976; Leventhal et al., 1986). Evidence of radiolysis can be apparent in petrographic analysis where vitrinite reflectance increases with U concentration (Breger, 1974). At a micro-scale, localised radiolytic damage can be seen by evidence of halo formation in the OM (and other material, e.g. silicates) which surrounds any U-bearing minerals (Gentry et al., 1976; Leventhal et al., 1987). As OM matures, the degree of loss of aromatic hydrocarbons (phenolic, OH etc.) can be measured though their H/C and O/C ratios (Court et al., 2006; Douglas et al., 2011; Jaraula et al., 2015; Kříbek et al., 1999; Landais et al., 1987). Radiolysis has also been connected to a decrease in overall bitumen yield and aliphatic hydrocarbons together with ^{13}C enrichment. Further indication of OM radiolysis has been linked to an increase in the number of aromatic, polar-hydrocarbon and asphaltene functional groups due to cleavage from larger OM moieties (Court et al., 2006; Dahl et al., 1988; Forbes et al., 1988; Landais, 1993; Zumberge et al., 1978).

2.2.3. Physical influences on OM

Thirdly, diagenesis of OM and accessory secondary U, from rising pressures and temperatures, contributes to mineralogical and chemical changes within OM deposits (Douglas et al., 2011; Wood, 1996). Under appropriate conditions Na-, K-, Mg-, V- and Ca-bearing clays may transform to kaolinites, and OM-rich sediments may transform into lignites, coals, bitumen and crude oils (for an evolutionary explanation of solid bitumen, see Mossman, 1999). These diagenetic products, such as lignite and bitumen, are known to contain up to 4–8% U (Alexandre et al., 2009; Alexandre and Kyser, 2006; Douglas et al., 2011; England et al., 2001; Ilger et al., 1987; Kříbek et al., 1999; Reynolds et al., 1982; Rouzaud et al., 1980). Specific case studies are documented in Table 1. Considerable evidence indicates that U can remain mobile within such settings under certain conditions (Banning et al., 2013; Regenspurg et al., 2010). Banning et al. (2013) suggest that U is mobile and can be redistributed from lignite seams through Tertiary sands and Quaternary

gravels into surface peat bogs. Here, U mobility was attributed to the slightly alkaline (>7.2 pH) conditions of the Quaternary groundwaters (Banning et al. 2013). Whilst U(IV) is relatively insoluble and immobile, U(IV) present as colloids represent an alternative scenario for U mobilisation without involving an oxidation state change (Dreissig et al., 2011; Wang et al., 2014a; Wang et al., 2014b).

2.3. Redox environments and the immobilisation of U within roll-front deposits

Uranium "roll front" deposits are found in some sedimentary sandstones (Gaboreau et al., 2005). Roll front deposits form an oxidation-reduction (redox) gradient between oxic and anoxic parts of permeable layers within sedimentary deposits, often as the result of groundwater mixing (Hobday and Galloway, 1999; Min et al., 2005; Yue and Wang, 2011). A redox interface develops between the two zones where the 'invading' groundwater brings in oxidised U(VI) and meets reducing conditions in saturated sediments (Fig. 1). Such anoxic sediments typically contain pyrite, hydrogen sulphide and carbonaceous materials confined within relatively impermeable layers (Ilger et al., 1987). Other redox-active elements have been noted to form in series along redox gradients from oxic to post-oxic (Sun and Puttmann, 1996; Thomson et al., 1993). In marine sediments a succession of metals from Mn, I, Fe, Se and Pt, Cu and Pb, V, Zn and Sb has been found (Thomson et al., 1993). In organic sediments Pb, Zn, Sb, Co, Ag and Cu were found in redox succession, with As, U and Mo found enriched throughout the lower sediments (Sun and Puttmann, 1996). Reduced Fe and S compounds are important components in roll front deposits as they enable electron shuttling to occur in redox reactions. From such reactions, U(VI) can be reduced to U(IV) and become immobilised through precipitation as U-oxides. The interface remains mobile as dictated by chemical reactions and groundwater flux. Roll-front deposits were more likely to have formed post-GOE, because previous redox reactions would have been limited by predominantly reducing conditions. Reductive precipitation facilitated by the presence of reducing chemical species is thus an example of a process through which U can become entrapped in sediments, although not necessarily permanently. Resulting U concentrations along the redox gradients can often be up to 0.25 wt.% (Gaboreau et al., 2005; IAEA, 2009; Nash et al., 1981). Where present, OM-rich sediments can also display roll front-like characteristics (Douglas et al., 2011; Vodyanitskii, 2011), and it has been suggested that biotic processes are prominent drivers of U reduction in these settings. Indeed, direct enzymatic U reduction by microbes will increase the rate of U immobilisation (Angiboust et al., 2012; Bargar et al., 2013; Min et al., 2005; Regenspurg et al., 2010). Further, a recent study has experimentally demonstrated the ability for microbes (and zero-valent Fe) to fractionate U isotopes under reducing conditions (Rademacher et al., 2006; Stirling et al., 2015). In view of this fractionation, possible reinterpretation of the geological record may be necessary due to the influence of biotic processes on U isotopic signatures.

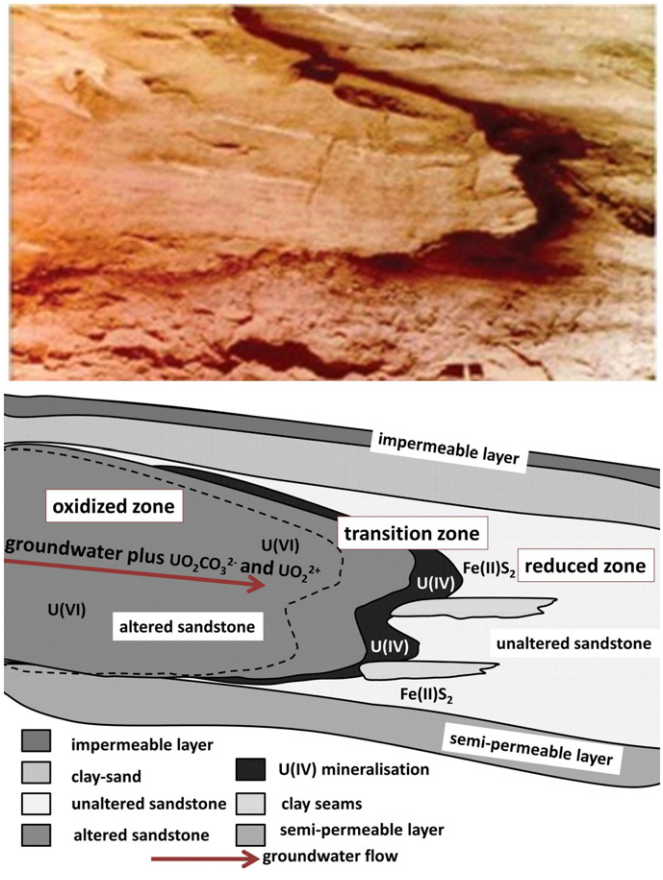


Fig. 1. Roll front deposit. Photograph showing reaction zone (taken from AREVA, published in Renard and Beucher (2012)). Image size represents approximately 8 m. Conceptual diagram of a uranium roll-front deposit in cross-section. Oxidised groundwater moves from left to right. The roll front associated interface moves in the same direction. Mineralised U(IV) precipitates along the transition zone as shown in black. Modified from Ilger et al. (1987), Yue and Wang (2011) and Langmuir (1997).

In the section above, low-temperature geological U biogeochemical cycling has been discussed. This process intensified globally after the GOE because as the rate of weathering of granitic (parent) rocks increased, more soluble and therefore increasingly mobile U compounds became available for transportation. This situation enabled new secondary deposits to be formed in sediments, often containing higher U concentrations than the source rocks. Over geological timeframes, these U bearing sediments may experience a range of processes, some of which modify the shorter (e.g. microbial activity) and longer term (e.g. diagenesis, oxidation state change within roll-fronts) stability of accumulated U. In the longer term, however, the stability of such U sinks may be modified via radioactive decay, and hence radiolysis of the OM. Understanding the geochemical and mineralogical histories of the palaeo-environmental settings within which U is deposited, and the processes by which these deposits can be subsequently altered, therefore requires consideration of the molecular scale biogeochemical processes shaping U mobility, entrapment, and stability in OM-rich sediments.

3. Uranium stability and mobility at the molecular scale

Within OM-rich sediments, the micro-level stability and mobility of U are primarily determined by geochemical processes that dictate the U oxidation state (Langmuir, 1997), the formation of soluble U compounds, including through competitive inorganic and organic ligand absorption and transport processes, and the precipitation and sorption behaviour of U and U complexes. This section reviews the mobility of U in terms of U oxidation state (Section 3.1), the solubility of U compounds in Section 3.2 and how U becomes immobile through precipitation and absorption in Section 3.3. Other influences on the chemistry and mobility of U are then discussed, including that of V, with Section 3.4 examining the relationship between U and Fe and Section 3.5 synthesising literature on U and OM. Elements such as Mn, As and REEs, that also contribute to the general redox environment are not discussed in detail, as they fall outside the scope of this review.

3.1. Oxidation states of uranium

The oxidation state of U is pivotal in determining its stability and mobility (Ray et al., 2011; Wellman et al., 2008). Naturally occurring U is dominated by U(IV) and U(VI) oxidation states, with tetravalent U having considerably lower solubility than hexavalent U, which is more soluble and more mobile. Uraninite and coffinite are the primary uranium U(IV) minerals which through weathering and oxidation forms

U(VI) compounds (or uranyl compounds). In contrast, valencies between U(0) and U(III) are highly unlikely to be found in the natural environment. U(III) has, however, been synthesised in the laboratory and shown to form complexes with organic compounds (Ferronsky and Polyakov, 2012; Kosog et al., 2012). The pentavalent U^V ion, although rare, can be found naturally. It is generally considered to form weaker, less stable complexes than U(IV), however, in reduced waters below pH 7, UO_2^+, may attain appreciable stability (Langmuir, 1978). A small number of studies have reported U^V as a short–lived intermediary, possibly microbially controlled (Renshaw et al., 2005) and perhaps able to exist between pH 2 and 4 (Chen et al., 2005). Whilst the existence of U(V) silicate [$K(UO)Si2O_6$] has been confirmed through laboratory synthesis (Arnold et al., 2009; Chen et al., 2005), a rare naturally occurring U(V) mineral, wyratite [$CaU^{5+}(UO_2)_2(CO_3)O_4(OH)(H_2O)_7$)], has been identified from both the Shinkolobwe Mine, Shaba, Democratic Republic of Congo and from the Ranger Mine, NT, Australia (Burns and Finch, 1999; Frost et al., 2004). Wyratite is thought to be an alteration product of uraninite which can readily oxidise to schoepite (Burns and Finch, 1999). Challenges in identification of U(V) from mixed valence (U(IV)/U(VI) compounds can arise in some techniques (e.g. position of the L_{III} edge energy in XANES). Essentially though, current U(V) identification lies in determining its coordination environment (Atta-Fynn et al., 2012; Burns and Finch, 1999). In order to fully appreciate the significance of U(V) in the environment, more detailed studies are therefore required to isolate distinguishing U(V) characteristics from those of U(VI) and U(IV) and to examine the relationship between U(V) and OM (Ilton et al., 2007; Kvashnina et al., 2013; Ulrich et al., 2009).

The change in oxidation state from U(IV) to U(VI) usually occurs in nature under oxidising conditions at the geosphere/atmosphere interface or within the lithosphere from contact with oxygenated groundwater (Murakami et al., 1997). Due to the ability for uraninite (UO_2) to host U(VI) oxidation states within its structure and around its edges, uraninite may persist in highly oxidising environments (Finch and Ewing, 1992). According to Zielinski and Meier (1988), oxidation of U(IV) in air is extremely slow even under low carbonate conditions. Alternatively, where uraninite has been formed under biogenic influences, it is considered to be more susceptible to oxidation (Alessi et al., 2014a; Campbell et al., 2011; Cerrato et al., 2013). The difference in oxidation rate is attributed to the disordered structure of the biogenic uraninite. Ginder-Vogel et al. (2010) also showed that the rate of oxidation of uraninite by Fe(III) was higher for biogenic than chemogenic uraninite. Sporadic oxidation of U(IV) to U(VI) could, however, have occurred from alpha-radiolysis prior to the GOE despite the anoxic atmosphere or from U radiogenic decay (Hazen et al., 2009). One explanation for the latter describes this oxidation state change as a result of U-daughter products having a different chemistry from surrounding U atoms (Hazen et al., 2009). Reports further suggest that alpha-radiolysis may be responsible for the appearance of U(VI) studtite [$UO_2(O_2)(H_2O)_2$] on the edge of uraninite under low oxygen conditions (Burns, 2005; Grenthe et al., 2011).

Uranium may therefore change from U(IV) to the more soluble U(VI), though this transformation is extremely slow under primary conditions in the absence of other catalysts. Burns (2005) describes 368 inorganic crystal compounds or structures containing U, of which 89 are naturally occurring minerals. Hazen et al. (2009) increased the number of U-forming minerals to 250. A summary of the low temperature U minerals identified in this review is presented in Table 2. The majority of these minerals have U in the +6 oxidation state. With the exception of occasional substitution of U for other cations in minerals, most U compounds are present as UO_2, UO_2^+ or UO_2^{2+} species. These molecules show variation in coordination environments, with U^{4+} forming single bonds with four oxygen atoms whilst U^{6+} forms double bonds with two oxygen atoms (i.e. UO_2^{2+}). Brannerite, ($UTiO_6$ (Ruh and Wadsley, 1966)), is thought to host U as U^{4+}, probably because formation of brannerite requires low pH and anoxic conditions, but may contain U^{4+}, U^{5+} and U^{6+} in a mixed oxidation state (Finnie et al., 2003; Vance et al., 2001).

The ability of U(IV) to bond with most inorganic ligands is the result of its strong hydrolysis potential (Berto et al., 2012; Grenthe et al., 2011). Variation in coordination number stems from a large ionic radius (0.93 Å), with coffinite ($USiO_4.nH_2O$) an example of eight-fold coordination in which U shares all of its oxygen atoms with silicate (Grenthe et al., 2011) although its true structure and formation is debated in the literature (Guo et al., 2015; Mesbah et al., 2015). Alternatively, U(VI), with small ligand complexes, forms pentagonal bipyramidal coordination, contrasting with that of the *d*-transitional and main-group elements (Burns, 2005; Grenthe et al., 2011). Octahedral or pentagonal bipyramidal structures can also be found in a number of oxides and uraninates (Grenthe et al., 2011).

3.2. Uranium phases and their solubilities

Whilst U(VI) is generally more soluble and therefore more mobile than U(IV), the solubility of U-bearing phases varies, even for compositions. Influential to both situations is pH; commonly the solubility of U(VI) phases increases in the presence of (bi)carbonate species, particularly above pH 5.5. However, U(IV) is sparingly soluble throughout the environmental pH range (Langmuir, 1978), except potentially at lower pH (i.e. <3), though this pH is more commonly associated with anthropogenic environments (e.g. acid mine drainage). It is also possible that U(IV) could be mobilised in a colloidal phase (Celine et al., 2009; Dosseto et al., 2006; Dreissig et al., 2011; Wang et al., 2014a; Wang et al., 2013), and therefore it is important to operationally define (e.g., <0.2 μm filter size) the solubility of U oxidation states. To reinforce this point, the following sub-sections discuss the solubilities of common U ionic groups: the oxides/hydroxides, carbonates, phosphates, silicates, sulphates and vanadates. In doing so, we review the current knowledge on solubility constants (log K_{sp}) where available (Gorman-Lewis et al., 2008a; Gorman-Lewis et al., 2008b; Grenthe et al., 2004; Langmuir, 1978) and draw contrasts between the potential mobility of different U compounds.

The inherent complexity of U speciation as a function of solution chemistry, in particular Eh, pH, and the presence of a range of common complexing anions, including SiO_4^{4-}, SO_4^{2-}, CO_3^{2-}, and dissolved organic carbon (DOC), is illustrated in Fig. 2 and Fig. 3. U speciation was determined in a 1/100 dilution model seawater solution using Geochemist's Workbench® (GWB) in Fig. 2 (Bethke et al., 2014; Bethke and Yeakel, 2014) and PHREEQC in Fig. 3 (Parkhurst, 1995; Parkhurst and Appelo, 1999).

In the simplest scenario, in the absence of important complexing ligands (e.g. carbonate, phosphate, sulphate, vanadate), U speciation is dominated by the UO_2^{2+} cation until ca. pH 4–5 whereupon a suite of UO_2-OH complexes dominate at circumneutral pH, showing $(UO_2)_3(OH)_7^-$ as the predominant species at a pH of ca. 7 and above (Fig. 2d). In all other cases where carbonates are present the $UO_2CO_3^{4-}$ is always dominate above ~pH 9. When viewed as a function of Eh in a Pourbaix diagram, uraninite is the predominate U mineral to precipitate in this system over a range of pH and at low to extremely low Eh (Fig. 2a–b, d–f). With the introduction of other ligands, a range of UO_2^{2+} species may be present at low pH/high Eh, in particular $U(VI)O_2SO_4$. The U(IV) species $U(SO_4)_2$ and $U(HPO_4)_4^{4-}$ are potentially present at low pH/low Eh, with $U(HPO_4)_4^{4-}$ also able to persist towards higher pH (Fig. 2a–f). In addition, a range of other U minerals including coffinite, carnotite, soddyite, haiweeite and saleeite are able to precipitate due to the presence of other ligands.

Of particular significance to U speciation is the influence of humic substances (see Fig. 3b). Whilst data on U complexation, particularly UO_2-humic substance stability constants, are scarce (Lenhart et al., 2000; Shanbhag and Choppin, 1981), published log K estimates are consistent, despite recognition of possible variation as a function of solute pH (Berto et al., 2012; Reiller et al., 2008; Schmeide et al., 2003; Steudtner et al., 2011; Zhu et al., 2014). This variation presumably is related to the progressive de-protonation of one or more of the

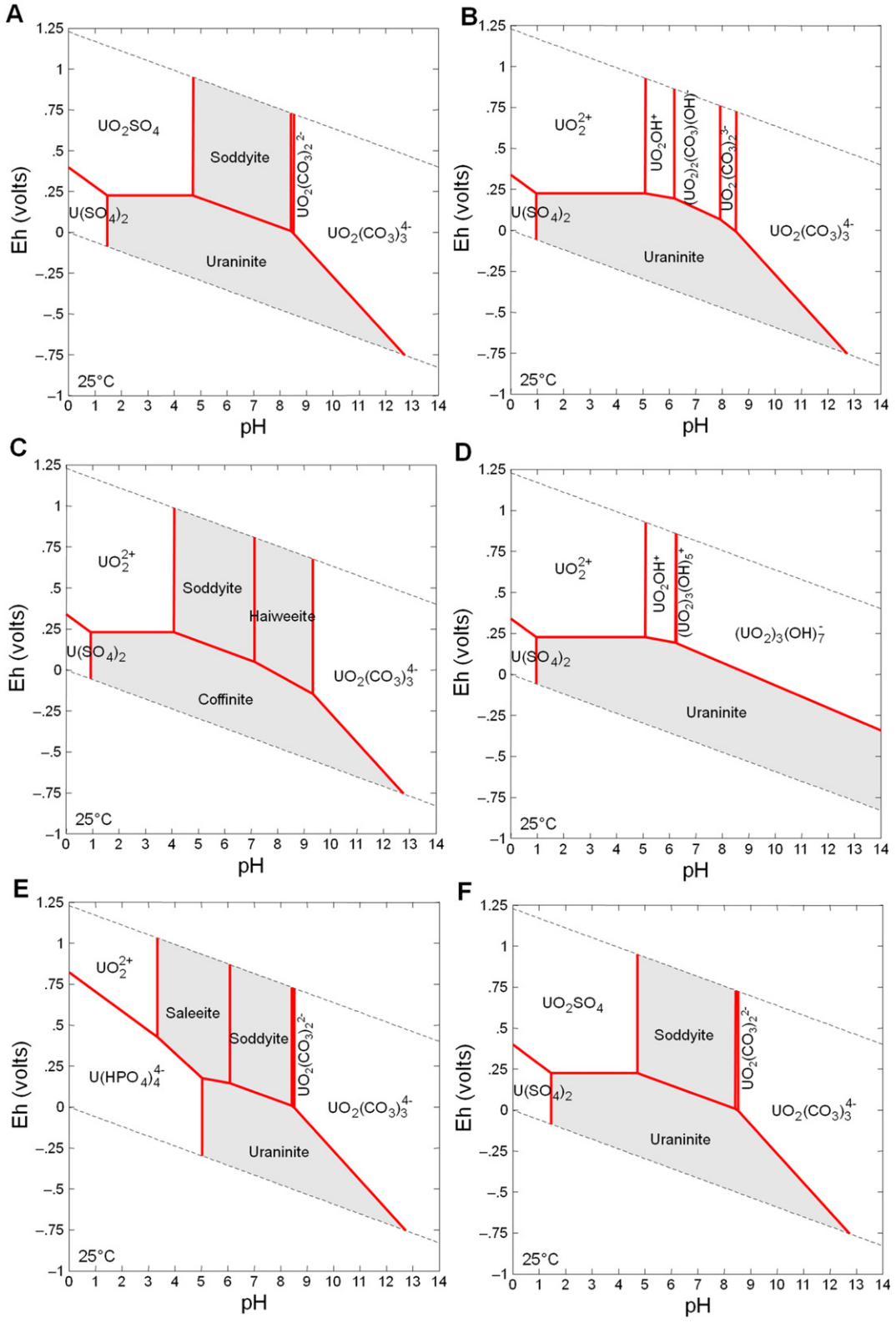


Fig. 2. Solution chemistry of uranium species as a function of pH/Eh. Calculations and images were created in Geochemist's Workbench® (thermo.dat database) (Bethke et al., 2014; Bethke and Yeakel, 2014) using the following conditions: concentration U 10^{-6} M: P_{CO2} $10^{-3.5}$; at 1/100 seawater concentration at 25 °C. (A) Aqueous species included: CO_3^{2-}, SO_4^{4-}, PO_4^{3-}, SiO_4^{4+}, UO_2^{2+}. The following were calculated as for (A) with adjustments as follows: (B) absence of SiO_4^{4+}; (C) with increased concentrations of SiO_4^{4+}; (D) absence of SiO_4^{4+} and CO_3^{2-}; (E) with higher PO_4^{3-} concentrations; (F) as for (A) but with increased SO_4^{2-} concentrations. The grey fields denote minerals and white fields denote soluble species. 1/100th seawater was used to include relevant calcium and carbonate complexes.

carboxylate, catechol and hydroxyl functional groups that occurs with increasing pH. Other factors that may cause variation in log K, and thus influence the extent of UO_2-humate bonding, are conformational changes in humics (also in response to pH) and the presence of other cations and UO_2-complexing anions. As illustrated in Fig. 3, humate, as a bidentate ligand appears to compete for dissolved U in the absence

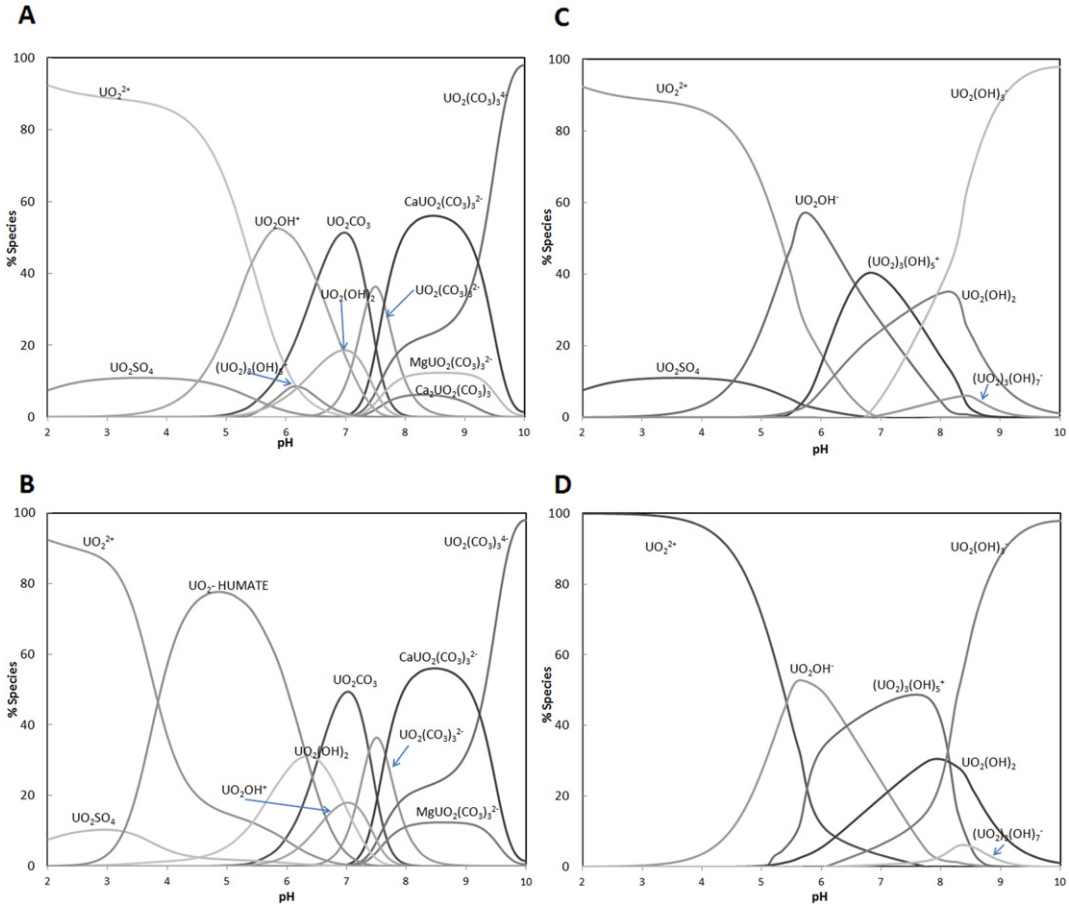


Fig. 3. Percent of uranium species for the following systems: (A) UO_2-H_2O-CO_2; (B) UO_2-H_2O-humate; (C) UO_2-H_2O-SO_4; (D) UO_2-H_2O. Modelled speciation generated using PHREEQC (Parkhurst, 1995) under the following conditions: concentration U 10^{-6} M: P_{CO2} $10^{-3.5}$; at 1/100 seawater concentration at 25 °C. Any species of <5% was not plotted.

of phosphate, particularly over pH 4 to 6. The significance of the UO_2-humate complex may effectively extend the mobility of U species across a much wider pH range with implications for enhancing or inhibiting U transport in OM-rich environments, depending on other factors (e.g., ionic strength, presence of other organic-metal complexes) influencing the solubility or aggregation state of the organic matter. Indeed, this was demonstrated in the modelling outcomes of Murphy et al. (1999), which showed U phenolic bonds dominated at pH 6 (Log $K = 1.63$). This can be considered similar to the UO_2-humate bonding at pH 6 seen in Fig. 3b. Murphy et al. (1999) also showed that an alternative UO_2-carboxyl bonding would be evident at pH 3.5 (Log $K = 2.39$).

3.2.1. Oxides and hydroxides

Uranium may form both dioxides and trioxides (e.g. UO_2, UO_3 and U_3O_8). A number of pure U oxides can be formed in both the U(IV) and U(VI) oxidation states, such as uraninite [UO_2] and schoepite [$(UO_2)O_2(OH)_{12}\cdot 12H_2O$] (Jang et al., 2006). Schoepite and metaschoepite [$UO_3(H_2O)_2$] are uranyl oxide hydrates that possess electroneutral sheets of uranyl pentagonal bipyramids with no interlayer cations (Gorman-Lewis et al., 2008a). Differences between the two minerals are apparent in the ratio of OH^- groups to UO_2^{2+} groups (Shvareva et al., 2012). The pitchblende trioxide U_3O_8, a stoichiometric mixture of UO_2, U_2O_6 and UO_3, forms an orthorhombic structure, within which all U atoms are coordinated with oxygen atoms to create pentagonal bipyramids (Grenthe et al., 2011).

The solubility of the U-oxides varies greatly depending on the oxidation state of U. The U(IV)O_2 is generally insoluble, with the solubility product of amorphous UO_2 determined by Warwick et al. (2005) as log $K_{sp} = -56.2 \pm 0.3$ over the pH range 7.0–10.4, which they concluded was in agreement with other studies. In contrast, U(VI) oxides and hydroxides are more soluble, with the solubility of schoepite, for example, reported as log $K_{sp} = 5.39$ by Langmuir (1978) – see Jang et al. (2006) for a more detailed discussion. Bruno and Sandino (1988) and Grenthe et al. (2004) give the solubility of schoepite as 1 to 17 mg UO_2^{2+} L^{-1} over pH range pH 6.8–8.3. The solubility of metaschoepite [$UO_3(H_2O)_2$] has been reported between a log K_{sp} of 4.68 and 6.23 (Gorman-Lewis et al., 2008a).

In the environment, U(IV) hydroxyl complexes (e.g. $U(OH)_5^-$), have been known to reach significant concentrations in alkaline groundwaters (>pH 8) (Langmuir, 1978). The natural persistence of the U(VI) uranyl hydroxyl compounds, however, remains less certain. Langmuir (1978) raises two considerations here: first, only monomers and dimers are significant, where the significant species have been shown to be UO_2^{2+}, UO_2OH^+, $(UO_2)_2(OH)_2^{2+}$ and $(UO_2)_3(OH)_5^+$; second, hydroxyl ion complexes become more important with increasing temperature, whereas the polymers are more prominent with the availability of dissolved U.

Due to the low solubility of U(IV) ore in water, acid leaching is commonly deployed in mining to extract U from non- or low-carbonate bearing ores (Taylor et al., 2004). In this type of extraction, solid phase U-oxides can be dissolved in HCl, H_2SO_4 or H_3PO_4 and U does not change oxidation state (Grenthe et al., 2011). In terms of other processes that enable U release, uraninite, for example, can be oxidised first to U(VI)O_2^{2+} in the presence of suitable oxidants, such as H_2O_2, and then to uranyl-oxide hydrates, such as becquerelite and schoepite, which can be subsequently dissolved (De Pablo et al., 1999; De Windt et al., 2003; Pierce et al., 2005). In natural settings, this can lead to the formation of U silicates (De Windt et al., 2003). During oxidative dissolution, where UO_2 is dissolved at neutral to alkaline pH, dissolution may proceed through intermediate stages (i.e., U_3O_7 or U_4O_9). This can be seen

by the formation of oxide layers as a coating around the core of UO_2 (Bi et al., 2013; De Pablo et al., 1999; Finch and Ewing, 1992). Oxidative dissolution has been described by Bi et al. (2013) to occur through a reaction sequence that progresses from oxygen adsorption, to activation of surface complexes and electron transfer, resulting in the subsequent release of U(VI) to solution.

3.2.2. Carbonates

In most oxygen-rich environments absent of OM, carbonate and/or phosphate complexes are likely to dominate U speciation. Carbonates (CO_3^{2-}) are important due to their ability to solubilise UO_2^{2+}, as carbonate complexes, thus increasing the likelihood of U mobility in alkaline conditions. Where ore consists of high proportions of U(VI) to U(IV) then a carbonate solution can be deployed to extract the ore either in above ground processing or in in-situ leaching (Hunkin et al., 1979; Mason et al., 1997; NRC, 2009; Rhoades, 1974). The most likely uranyl-carbonate species to form is the $UO_2(CO_3)_3^{4-}$, whilst $CaUO_2(CO_3)_3^{2-}$ and $Ca_2UO_2(CO_3)_3^0$ will form providing that the solution has significant Ca^{2+} cations (Banning et al., 2013; Dong and Brooks, 2006; Elless and Lee, 1998; Langmuir, 1978; Stewart et al., 2011; Stewart et al., 2007). The formation of these abovementioned species is indicative of the greater influence that dissolved CO_2 has on the solubility of uranyl ions, than (higher) pH alone (Zhou and Gu, 2005).

Carbonate can also form minerals with U(VI). In a review paper by Gorman-Lewis et al. (2008a), rutherfordine [UO_2CO_3], was the least soluble of the uranyl carbonates (logK_{sp} between −13.2 to −15). Lower conditional solubility product constants are indicated for bayelite, liebigite, grimselite, andersonite and swartzite (−36.6 to −37.9 log K_{sp}), with schröckingerite reported at −85.5 log K_{sp} (Gorman-Lewis et al., 2008a; O'Brien and Williams, 1983). Gorman-Lewis et al. (2008a), however, raise concern over the methods used in deriving these values. For other U-CO_3^{2-} solubilities see Grenthe et al. (2004), and for speciation diagrams see Fig. 2 and work by Krestou and Panias (2004). It should be noted that the log K_{sp} values presented here (and in the following sub-sections) are conditional equilibrium constants for which the reader should consult the original references to obtain more information about how they were derived. The importance of carbonate chemistry in groundwater was demonstrated by Elless and Lee (1998) who established strong correlations between both groundwater U concentration and time ($R^2 = 0.97$), and alkalinity (an indirect measure of CO_3^{2-}) and time ($R^2 = 0.93$). In these situations the CO_3^{2-} ion acts as a strong chelator and can readily mobilise U(VI), even in the absence of oxygen. Furthermore, CO_3^{2-} may dissolve (and therefore solubilise) U(IV) by means of an oxidation state change under high oxidising conditions (Langmuir, 1978; Zhou and Gu, 2005).

3.2.3. Phosphates

In the absence of substantial carbonate, phosphate may form complexes with U. Uranyl phosphates, although able to compete for uranyl ions with CO_3^{2-} and VO_4^{3-}, are often less soluble than uranyl carbonates or silicates, but more soluble than vanadates (Breit and Wanty, 1991). They therefore represent an important group in terms of U ore formation. Within groundwater, the presence of phosphate minerals can also retard U mobility (Buck et al., 1996; Pinto et al., 2012; Wellman et al., 2012; Wellman et al., 2008). The lower solubility of uranyl phosphates has led to various phosphate–based compounds being commercially developed and deployed as lixiviates for U capture. Despite their importance, there is paucity of data on U-phosphate solubility with many inconsistencies in the literature (Reiller et al., 2012). The general lack of environmentally relevant data warrants further investigation, particularly where it involves OM (Sandino and Bruno, 1992). On account of this characteristic of the U-phosphates, many solubility experiments have been performed under unrealistic environmental conditions of high acidity and at high ionic strength (Gorman-Lewis et al., 2008a; OECD-NEA, 2012; Shvareva et al., 2012). The few solubility values that are available range between −53.33 log K_{sp} for uranyl orthophosphate to −12.17 log K_{sp} for uranyl hydrogen phosphate, with many products stated as insoluble (Gorman-Lewis et al., 2008a). The solubility for autunite [$Ca(UO_2)_2(PO_4)_2 \cdot 3H_2O$]·was reported to be −48.36 log K_{sp} (Gorman-Lewis et al., 2009). The impact of phosphate chemistry on U solubility is substantial, and not well understood (OECD-NEA, 2012). Nevertheless, some data have been reported on the solubility and molecular association of two uranyl phosphate (U–HPO_4 and U–polyphosphates) complexes (Vazquez et al., 2007). Vazquez et al. (2007) found that the solubility of U-phosphates varied substantially with pH. Under conditions pH < 6 an insoluble U–HPO_4 complex was formed, but when pH > 6, U-hydroxide precipitation predominated over U-phosphate resulting in the formation of an insoluble mixed-phase U–hydroxophosphate species. In contrast, a U-polyphosphate complex showed a greater solubility over the pH range; precipitation occurred below pH 5, whereas above pH 6, solubility increased.

3.2.4. Silicates

In general, the uranyl silicates have lower solubilities than uranyl carbonates or uranyl oxy-hydrates at circumneutral pH values, but are more soluble than uranyl phosphates (Finch and Ewing, 1992; Gorman-Lewis et al., 2008a; Gorman-Lewis et al., 2007; Maher et al., 2012). Uranyl silicates can be formed from either uranyl ions or U oxides; providing Si is present in solution and in excess of other competing aqueous ligands. Coffinite [$USiO_4$] is the most common U(IV) silicate and is thought to be derived from uraninite. Hexavalent uranyl silicate compounds, which include soddyite [$(UO_2)_2(SiO_4)(H_2O)_2$], boltwoodite [$(Na,K)(UO_2)(HSiO_4)\cdot H_2O$] and uranophane [$Ca(UO_2)_2(HSiO_4)_2\cdot 5H_2O$], are important minerals associated with the alteration of spent nuclear fuel under moist, oxidising conditions (Shvareva et al., 2011). Uranophane is the most common natural uranyl silicate (Langmuir, 1978). Shvareva et al. (2011) reported comparative solubilities for uranophane as 10.82 log K_{sp}, Na-boltwoodite as 6.07 log K_{sp} and boltwoodite as 4.12 log K_{sp}. The difference between boltwoodite and Na-boltwoodite is due to interlayer cations from Na which increases solubility (Gorman-Lewis et al., 2008b; Shvareva et al., 2011). Solubility products of soddyite have reported to range between 2.5 to 6.36 log K_{sp}, with synthetic soddyite calculated at 6.43 log K_{sp} (Gorman-Lewis et al., 2007).

3.2.5. Sulphates

Uranyl ions are less likely to form complexes with sulphates than with other anions reported above. Uranyl sulphates demonstrate extremely negative solubility products, with zippeite, for example, reported ranging between −116.1 and −153.0 log K_{sp}, although data were not adjusted for ionic strength effects (Gorman-Lewis et al., 2008a). Better quality data through more rigorous testing are required, especially as U-sulphates are environmentally widespread (Gorman-Lewis et al., 2008a). Uranyl sulphates are most relevant in acidic environments (see Figs. 2f and 3c), and are prevalent in acid-mine conditions as $UO_2SO_4^0$ and $UO_2(SO_4)^{2+}$ complexes. (Langmuir, 1978; Zammit et al., 2014; Brugger et al., 2003; Vodyanitskii, 2011). Whilst a detailed discussion of mining activities falls outside the scope of this review, the contaminants that arise from extractive processes represent important considerations for U mobility in the environment (Catalano et al., 2006; Ilton et al., 2006; McKinley et al., 2006; Simpson et al., 2006; Tokunaga et al., 2004; Um et al., 2009; Wan et al., 2004a; Wan et al., 2004b; Zachara et al., 2007).

3.2.6. Vanadates

The uranyl vanadates represent an important group because V and U are frequently found together within deposits (Hostetler and Garrels, 1962), including OM-rich deposits (Fishman et al., 1985; Shawe, 2011; Wood, 1996). Their relative solubility varies with respect to the above-mentioned U-minerals (Elless and Lee, 1998; Gustafson, 1949; Langmuir, 1978). Vanadium like U, is redox sensitive and has several oxidation states (III, IV and V) which determine its solubility. As with U,

reduced states have lower solubility than the oxidised states (Breit and Wanty, 1991; Miao et al., 2013). In the absence of U and OM, V generally forms either insoluble oxides (vanadates), very soluble chlorides (vanadiferous chlorites) or V^{III} hydroxides (e.g. montroseite, VO(OH)) (Hansley and Spirakis, 1992; Tokunaga et al., 2012; Wanty and Goldhaber, 1992).

Under conditions relevant to U geochemistry, V species are prominently present as $H_2VO_4^-$, HVO_4^{2-} and VO^{2+} in natural waters, particularly where $V < 10^{-4}$ M. Accordingly, the V(V) species predominates in oxidised waters (Langmuir, 1978), and in this state can combine with U, whereas V(IV) occurs within less oxygenated conditions (Hostetler and Garrels, 1962) and V(III) is observed in highly reduced conditions. Whilst much is known about V geochemistry (Kanamori and Tsuge, 2012; Langmuir, 1978; Wanty and Goldhaber, 1992), the study of U-vanadates has been limited (Tokunaga et al., 2012). This is despite recognition of U–V minerals in the literature, in particular the three most common: carnotite [$K_2(UO_2)2V_2O_8 \cdot 3H_2O$], tyuyamunite [$Ca(UO_2)2V_2O_8 \cdot 8H_2O$] and meta-tyuyamunite [Ca-$(UO_2)2V_2O_8$ 3 − $5H_2O$] (Elless and Lee, 1998; Gustafson, 1949; Langmuir, 1978). In general, U–V minerals are considered insoluble, with their degree of solubility affected by pH. Hostetler and Garrels (1962), for example, reports a solubility of 3×10^{-7} M L^{-1} at 25 °C for carnotite which is most soluble around pH 7–8 (Langmuir 1978, Hostetler and Garrels, 1962). Tyuyamunite, which has greater solubility than carnotite, displays a minimum solubility of 1 ppb U at around pH 7 (Langmuir 1978) (see Fig. 4). Carnotite does continue to increase in solubility above pH 7–8, however, competition from carbonates may instead lead to the formation of U-CO_3 complexes (Langmuir 1978). Langmuir (1978) further compared the ion activity products (IAP) of carnotite and tyuyamunite to their solubility products (K_{sp}), which yielded an average log (IAP/K_{sp}) of -0.9 ± 3.8 ($\pm = 2$ sd) for carnotite ($K_{sp} = 10^{-56.9}$) and 0.4 ± 3.8 for tyuyamunite ($K_{sp} = 10^{-53.4}$).

3.3. Uranium phases and pathways towards immobilisation

In contrast to Section 3.2, which investigated U phases and their solubility, Section 3.3 introduces potential pathways through which U-ions may become immobile. Included within these pathways are processes of precipitation and adsorption, both leading to the formation of solids. In the case of precipitation, U compounds may be embedded within insoluble solids formed through the reaction of solutes (or small particles), whereas adsorption involves U compounds being complexed at mineral-water surfaces. The theory behind the physicochemical interactions that allow solutes to adhere to small particles and/or mineral surfaces, and the strength of the 'sticking factor', is well developed (Lead and Wilkinson, 2007; Stumm and Morgan, 1996). It is the viability of these connections under different conditions and competitive scenarios that is considered in this sub-section. Three important factors should be noted. First, because U oxides and U hydroxyl complexes are potentially unstable, it is more likely that U-species will form complexes with other anions and that these complexes will drive the sorption and precipitation of U. Further detail on the aquatic U oxides and hydroxides, their bond lengths and coordination structures are presented in a review by Knope and Soderholm (2012). Recent advances in actinide thermodynamics are described by Altmaier et al. (2013). Second, the predominance of the carbonates on U chemistry under alkaline conditions must be acknowledged. Third, in view of the complex interactions among: ion competition; the electrostatic interactions between molecules; and solution ionic strength, surface complexation models (SCM) have been used to predict outcomes. This review will return to SCM in Section 4.

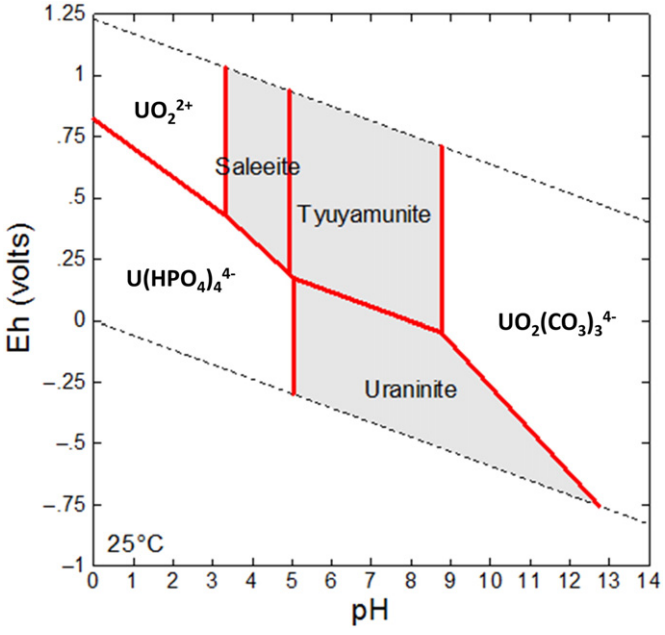


Fig. 4. Eh-pH speciation diagram for a system containing U, C, P, Si and V in a 1 in 100 seawater matrix calculated using Geochemist's Workbench® (thermo.dat database) with U 10^{-6} M: P_{CO2} $10^{-3.5}$; at 1/100 seawater concentration at 25 °C. The grey fields denote minerals and the white fields denote soluble species.

3.3.1. Carbonates

Uranium readily forms carbonate complexes at intermediate to high pH (Figs. 2 and 3). This association has implications for exploration (Min et al., 2000; Mossman, 1999), extraction (Adam et al., 2010; Bruggeman and Maes, 2010; Buck et al., 1996; Zhou and Gu, 2005) and U mine waste recovery (Santos and Ladeira, 2011). Conversely, the high affinity of UO_2^{2+} for carbonate can result in adsorption to carbonate mineral surfaces, such as calcite [$CaCO_3$] and dolomite [$CaMg(CO_3)_2$] (Elless and Lee, 1998; Kelly et al., 2006; Rihs et al., 2004), which could lead to immobilisation and enrichment. Kelly et al. (2006) examined 220 Ma U enriched calcites using X-ray fluorescence microscopy and discovered that U was present as U(VI). The authors proposed that U sorption occurred during the formation of the calcites by mechanism of U bonding to CO_3^{2-} ions as there was no evidence of U valence change. In the presence of $CaCO_3$, U(VI) forms a stable uranyl-triscarbonate-calcium complex that was considered resistant to microbial reduction in the ancient calcites studied (Kelly et al., 2006). A di-calcium uranyl carbonate, $Ca_2UO_2(CO3)_3$, was also observed by Bernhard et al. (2001) to exist within mining waters, with the aqueous form considered to be structurally similar to the mineral libigite.

The aforementioned affinity of UO_2^{2+} to carbonate also results in an increase in U solubility, particularly as pH increases (>5.5) and begins to dominate systems when pH > 6 (Krestou and Panias, 2004). In solution, uranyl carbonate complexes may prevent U(VI) adsorption onto surfaces (Beazley et al., 2011). Below pH 5.5 U-hydroxyl species are more prominent. When the pH range is between 6 and 8, the aqueous U species, $UO_2(CO_3)_2^{2-}$ predominates (see Fig. 2). For pH higher than 8, U(VI) complex ions are transformed to the more stable $UO_2(CO_3)_3^{4-}$ ion, as seen in Fig. 2, agreeing with the modelled "open system" of Krestou and Panias (2004). The presence of carbonates can increase U mobility in soils and offsets any other inherent soil properties preventing sorption to anionic and amphoteric sites of clay minerals under alkaline conditions (Echevarria et al., 2001; Elless and Lee, 1998). Under these conditions U forms highly mobile negatively charged carbonate complexes, such as $UO_2(CO_3)_2^{2-}$ or $UO_2(CO_3)_4^{3-}$ (Elless and Lee, 1998). Similarly, the sorption results of Zielinski and Meier (1988) suggested that peat was unable to concentrate U in a carbonate-rich environment. In the same set of experiments, Zielinski and Meier (1988) found CO_3^{2-} to be an excellent extractor of U from peaty substrates.

3.3.2. Phosphates

Uranyl phosphate complexes are another important group influencing the environmental fate and behaviour of U (Sandino and Bruno, 1992). Like carbonates, phosphates have a high affinity with U, but are more likely to be mineral forming (Mehta et al., 2014). As a result, soluble U species may form secondary deposits after the dissolution of primary uraninite (e.g. Wycheproof granites, (Birch et al., 2011)). The presence of soluble uranyl phosphates within water streams therefore has relevance to U exploration (Jerden and Sinha, 2006). Similarly, rock phosphate deposits frequently mined for agricultural fertilizers can contain appreciable concentrations of U, potentially leading to U enrichment within soils and food outputs (Adam et al., 2010; Alloway, 2013; Schipper et al., 2011).

Uranyl-phosphates are commonly found alongside Fe-oxyhydroxides, whereby U absorbed on the surface of the FeOOH becomes available for PO_4^{3-} complexation (Buck et al., 1996; Jerden and Sinha, 2006; Mills et al., 2008). Autunite (Ca), meta-autunite, torbernite (Cu), meta-torbernite and selenite (Mg) are the principle uranyl phosphate minerals. U-PO_4 crystal structures and their bond lengths have been extensively studied by Burns and co-workers (Burns, 1999; Burns, 2005; Burns et al., 1997; Locock and Burns, 2003; Wylie et al., 2012). The Ca-U-phosphate mineral, autunite, is likely to have been formed through the interaction between apatite [$Ca_5(PO_4)_3(F,Cl,OH)$] and oxidised uraninite/coffinite. The crystal structure of autunite shows that U and P occur in a 1:1 ratio, and crystallise in the tetragonal or pseudotetragonal structures (Buck et al., 1996; Pinto et al., 2012), whereas the phosphuranylites [$KCa(H_3O)_3(UO_2)_7(PO_4)_4O_4\cdot 8H_2O$] form U:P ratios of 3:2 and crystallise in a orthorhombic fashion as parallel sheets (Pinto et al., 2012).

Importantly, phosphates and carbonates directly compete for U (Beazley et al., 2011). Carbonates may react with uranyl phosphates as uranyl ions with a tendency to form soluble carbonate complexes above pH 6–7 (Zhou and Gu, 2005). The U-phosphates may therefore dissociate where carbonates are present leading to increased U mobility in the form of U(VI) carbonate complexes. This process is described in Eq. (1) for calcium uranyl phosphates (Buck et al., 1996).

$$Ca(UO_2)_2(PO_4)_{(s)} + 3CO_3^{2-} + H2O \leftrightarrows UO_2(CO_3)_3^{4-} + Ca^{2+} + HPO_4^{2-} + 2OH^- \quad \text{(Eq. 1)}$$

3.3.3. Silicates

Uranyl-silicate U(VI) minerals are important constituents in the oxidised zones of U ore deposits. Silicates are less competitive for U ions than either CO_3^{2-} or PO_4^{3-}, but nevertheless are important where silicates are present in sufficient concentrations. Uranyl silicates may in general only form and persist in waters where the activity of dissolved silica in groundwater as H_4SiO_4 (aq) is $\geq 10^{-3.7}$; pH < 9 (De Windt et al., 2003; Finch and Ewing, 1992). Under such conditions, uranyl silicates, as secondary alterations on primary minerals, have been found on uraninite and coffinite surfaces as a result of oxidation processes (Deditius et al., 2008; Finch and Ewing, 1992; Isobe et al., 1992; Shvareva et al., 2011). Uranyl-silicate minerals may occur in both the U(IV) and the U(VI) oxidation states, with U(IV) coffinite and U(VI) uranophane and boltwoodite the most common. Coffinite may undergo several phase changes and thus could be present within deposits as either primary or secondary minerals. Physico-chemical properties and crystal structures of coffinite have been reported by Dreissig et al. (2011), Gorman-Lewis et al. (2007) and Pointeau et al. (2009). However, since its discovery in 1955 (Fuchs and Gebert, 1958; Stieff et al., 1955; Stieff et al., 1956) the actual structure of coffinite has been extremely hard to both define and synthesise despite being commonly reported in organic-rich environments (Guo et al., 2015; Mesbah et al., 2015).

Organic matter may also influence uranyl silicate speciation, and uranyl-silicate colloids formation. More explicitly it has been suggested that: (1) U-silicates may be dependent on OM for formation (Deditius et al., 2008); (2) OM may play an important role in U-silicate chemistry by shielding U(IV) minerals (such as coffinite) from oxidising conditions (Deditius et al., 2008); and (3) OM may promote the formation and stability of colloidal forms of U-Si. In generic metal-colloid formation, the capability of natural organic matter (NOM), such as humic substances, to coat and stabilise other metal colloids has been demonstrated (Cumberland and Lead, 2009; Cumberland and Lead, 2013). The laboratory-based synthesis of U-Si colloids has been reported by Dreissig et al. (2011). Should such formations occur in the environment then the role that OM might play in stabilising and/or mobilising U requires further investigation. Dreissig et al. (2011) also investigated U-Si colloidal structure by using extended X-ray absorption fine structure (EXAFS) and noted that U-O-Si bonds had formed from Si replacement of the U-O-U bonds of the amorphous U(IV) oxyhydroxide.

3.3.4. Sulphates

Uranium-sulphates are another group of species and minerals which influence U solubility and deposition (Bowie, 1979). Fifteen known minerals constitute this group, the three most environmentally important are: zippeites [$M_2(UO_2)_6(SO_4)_3(OH)_{10}\cdot(H_2O)_n$]; M=Mg, Co, Ni and Zn; johannite [$Cu(UO_2)_2^-(SO_4)_2(OH)_2\cdot H_2O_8$]; and uranopilite [$(UO_2)_6(SO_4)O_2^-(OH)_6\cdot(H_2O)_6$] (Burns, 2001; Burns, 2005; Gorman-Lewis et al., 2008a; Hazen et al., 2009). Although processes of uranyl sulphate formation may be predominantly abiotic, studies have focused on bio-reduction by sulphate-reducing bacteria, with such reactions also likely to include NO_3^- and Fe(III) reduction redox (Law et al., 2011; Ray et al., 2011; Salome et al., 2013).

3.3.5. Vanadates

Uranyl vanadates are an important group of ions and minerals capable of influencing U under a range of environmental conditions. Isostructually similar uranyl vanadates include carnotite [$K_2(UO_2)(V_2O_8)\cdot 3H_2O$], tyuyamunite [$Ca(UO_2)(V_2O_8)\cdot 9H_2O$], metatyuyamunite [$Ca(UO_2)(V_2O_8)\cdot 3H_2O$], strelkinite [$Na_2(UO_2)(V_2O_8)\cdot 6H_2O$], curienite [$Pb_2(UO_2)(V_2O_8)_5H_2O$], francevillite [$Ba,Pb(UO_2)(V_2O_8)\cdot 5H_2O$] and vanuralite [$Al(OH)(UO_2)_2(V_2O_8)\cdot 3H_2O$] (Frost et al., 2005), with carnotite being the most common. Similarities between these U-V minerals stem from interlayered cation (e.g. Ca, K, Na, Ba) positioning with the V atoms coordinated by five oxygen atoms giving a layer constructed by $((UO_2)2V_2O_8)n)2n$ units ((Frost et al., 2005), see also (Jouffret et al., 2010; Kanamori and Tsuge, 2012)). A hypothetical groundwater system that contains U, C, P, Si and V in a 1 in 100 seawater matrix as a function of pH and Eh is shown in Fig. 4. It indicates the possible formation of tyuyamunite at circumneutral pH and where Eh is positive. This highlights that at circumneutral pH U-V minerals are predominant over uranyl hydroxides, as seen in Fig. 2.

Precipitation of carnotite has been found to form after potassium metavanadate (KVO_3) has been added to U(VI) solutions and will be further promoted under oxidising conditions between pH 4–8, in absence of CO_3^{2-} (Campbell et al., 2014; Tokunaga et al., 2009). Alternatively, where P is present in much higher concentrations than V, autunite results (Dongarra, 1984). According to Langmuir (1978), carnotite precipitation is likely to occur where CO_2-rich groundwaters equilibrate with atmospheric CO_2 levels at the land surface. Alternatively, V can be added to aquifers to precipitate U as carnotite or tyuyamunite, providing the pH remains below pH 7.5 (Campbell et al., 2014). Thus, precipitation of U(VI) via either carnotite or tyuyamunite can be achieved through pH neutralization (Tokunaga et al., 2009).

3.4. Uranium – iron chemistry

Iron is the fourth most abundant element within the earth's crust, a redox element and an essential component in microbial metal cycling (Roden, 2003; Weber et al., 2006). The general reactivity of Fe

significantly influences U chemistry, as seen in roll-front deposits. Iron, as Fe(II) and/or Fe(III), forms mostly oxide, oxyhydroxide and S-mineral compounds with Fe substitution in U-minerals common. Uraninite, for example, is known to contain Fe impurities, and brannerite [$UTiO_6$], can substitute Fe for U (Bowell et al., 2011; Colella et al., 2005; Fayek et al., 2011; Finnie et al., 2003; Ruh and Wadsley, 1966; Vance et al., 2001). Uranium-Fe minerals are less common than U-oxides and U-anions; nevertheless a small number do exist, including bassetite [$Fe((UO_2)(PO_4))_2(H_2O)_8$] and deliensite [$Fe(UO_2)_2(SO_4)_2(OH)_2(H_2O)_3$] (Deditius et al., 2008). Whilst Fe is less likely to form structural bonds with U or UO_2 compounds because of incompatibilities (Vodyanitskii, 2011), it remains highly influential in terms of U chemistry (Bruggeman and Maes, 2010). Two processes affecting UO_2 behaviour and speciation are adsorption to Fe surfaces and redox (Cheng et al., 2004; Cheng et al., 2006; Cheng et al., 2007; Du et al., 2011; Ginder-Vogel et al., 2010; Jang et al., 2008; Latta et al., 2012; Liger et al., 1999; O'Loughlin et al., 2003; Waite et al., 1994). Both are discussed below.

Uranium adsorption onto Fe mineral surfaces is pH and ionic strength dependant (Behrends et al., 2012; Duff et al., 2002; Stewart et al., 2011; Zhao et al., 2012). U(IV) absorption onto hydrous ferric oxides was reported to be pH 5–8 (Ulrich et al., 2006) and sorption of U(VI) onto hematite (Fe^{III} oxides, α-Fe_2O_3) was maxima at pH 6.0, with ionic strength only having an influence at low pH (Zhao et al., 2012). Bargar et al. (2000) found the bonding predominantly bidentate with two surface oxygen atoms complexing to U(VI). Waite et al. (1994) noted a similar bidentate bonding between U(VI) and ferrihydrite. Ferrihydrite can sequester many actinide ions, including UO_2^{2+}, although the impact (promotion or retardation) of common impurities found within natural ferrihydrite (e.g. Al^{III}, As, Si^{IV}) on sequestration is not known (Maher et al., 2012). It has been further shown that Al impurities can affect U sorption to ferrihydrite due to surface incompatibility (Massey et al., 2014). Aluminium also appeared to interfere in the transformation of ferrihydrite oxidation to goethite, which is more favoured for U sorption.

Iron mineral surfaces are likely to behave as catalysts through ion exchange or reaction sites, but require the proximity of reactive surfaces for redox reactions to occur (Jang et al., 2008). Accordingly, rather than reaction in aqueous, U must initially adsorb to such sites prior to precipitation or sequestration, as has been observed with U-PO_4 in Fe-rich soils (Jerden and Sinha, 2006; Sato et al., 1997). Furthermore, the presence of adsorbed ions and localised pH may affect surface reactivity (Zhao et al., 2012). In terms of U chemistry, Ahmed et al. (2012) showed that U-CO_3 and U-Ca-CO_3 do not adsorb as readily to mineral surfaces when compared to U-OH compounds due to dominance of the carbonate ion (Villalobos et al., 2001). A recent study by Alam and Cheng (2014) identified that Fe-Mn (oxy)hydroxides were important for hosting U-minerals in sediments and that U release aside from pH, was conditional on bicarbonate, citrate and natural OM concentrations. In a number of studies, humics were shown to affect U-sorption to ferrihydrite surfaces only at low pH where sorption was enhanced (Lenhart et al., 2000; Lenhart and Honeyman, 1999; Payne et al., 1996).

The potential for Fe compounds to change the oxidation state of U has been investigated using a number of Fe oxides (e.g. ferrihydrite, goethite and hematite (Boyanov et al., 2007; Ginder-Vogel et al., 2010; Jang et al., 2008; Latta et al., 2012; Liger et al., 1999; Stewart et al., 2011; Stewart et al., 2007)), Fe sulphides (e.g. pyrite and mackinawite (Bargar et al., 2013; Bi et al., 2013; Carpenter et al., 2015; Gallegos et al., 2013; Hyun et al., 2012; Lee et al., 2013; Veeramani et al., 2013)) and zero-valent iron (i.e. nanoparticles) (Cantrell et al., 1995; Crane et al., 2015; Gu et al., 1998; Li et al., 2015b). Ferrihydrite exists exclusively as Fe(II/III) nano-crystals (Cornell and Schwertmann, 2003), and therefore has an inherently large surface area. Compared to goethite (α-FeOOH) and hematite, ferrihydrite has a high redox potential (Stewart et al., 2011) and may either compete as an electron acceptor in microbial respiration or act as an oxidant of biogenic UO_2. Uranium reduction from U(VI) to U(IV) occurs abiotically when Fe(II) is simultaneously oxidised to Fe(III) (Boland et al., 2014; Du et al., 2011; Latta et al., 2012; O'Loughlin et al., 2003; Percak-Dennett et al., 2013). The degree to which this happens is influenced by factors including: the amount of Fe(II) available in mixed Fe(II/III) compounds; the extent of biotic reduction by Fe-reducing/oxidising bacteria (Behrends and Van Cappellen, 2005; Wilkins et al., 2006); the presence of ions such as Ca^{2+} and CO_3^{2-}; and OM (Jang et al., 2008; Stewart et al., 2011).

When Fe(II) has been applied to sediments as a reducing agent for U(VI), in several studies it has been observed to rapidly become depleted and for U(VI) reduction to decline (Moon et al., 2007; Wilkins et al., 2006). With the addition of Fe(III) to sediments it has been further shown that rates of U(VI) reduction were enhanced (Anderson et al., 2003; Jeon et al., 2005; Spycher et al., 2011; Wilkins et al., 2006) and that bacterial communities were maintained (e.g. *Geobacter* sps.) (Lovley et al., 1993; Moon et al., 2007; Moon et al., 2010). This simultaneous reduction of Fe(III) and U(VI) was explained in the work of Behrends and Van Cappellen (2005), who indicated through batch experiments that reduction of U(VI) by Fe(III) was promoted by *S. putrefaciens* that were reducing Fe(III) to Fe(II), with the Fe(II) product then acting as a reductant for U(VI). In other studies, microbially reduced U(IV) has been observed to re-oxidise in the presence of Fe(III) (Sani et al., 2005; Wan et al., 2005). The role of Fe in U(VI) reduction mediated by microbial direct enzymatic reduction has been reviewed by Wilkins et al. (2006).

The presence of SO_4^{2-} also provides alternative pathways via the production of FeS as pyrite or mackinawite (Lee et al., 2013). Biotically produced mackinawite is able to reduce U(VI) to U(IV) under abiotic conditions (Gallegos et al., 2013; Hyun et al., 2012). However, some remobilisation of the U product has also been seen to occur due to the production of nanoparticles (Lee et al., 2013; Veeramani et al., 2013). The supply of (additional) OM (humics, acetate, lactate etc.) helps maintain reducing conditions by providing electron donors for microbes, thus limiting the likelihood that previously reduced U(IV) compounds are re-oxidised (Campbell et al., 2012).

3.5. Influences of organic matter on uranium chemistry

In addition to the oxidation state of U, anion chemistry, pH, and the presence of Fe, another influential factor shaping U stability and mobility is the interaction of U with OM. To understand the importance of OM in influencing U chemistry, we describe the characteristics of OM, discuss current evidence relating to U-OM bonding and synthesise literature on U-OM sorption and U relationships.

3.5.1. OM characteristics

Natural organic matter (NOM) consists of an intricate mixture of organic compounds, often different in composition and functionality (Amy and Cho, 1999; Croué, 2004; Croué et al., 1998; Croué et al., 1999; Frimmel, 1998). These compounds derive from decomposing OM or from anthropogenic inputs (Frimmel, 1998). In the aquatic environment, much of the colloidal fraction (1–1000 μm) is made up of various NOM types including microorganisms, extra-cellular polysaccharides and dissolved organic carbon (DOC) (Thurman, 1985). The NOM plays a vital role in aquatic ecosystems, affecting the physicochemical properties of water (Croué et al., 2000), nutrient and carbon cycling, and the bioavailability of trace metals (Croué et al., 1993; Frimmel, 1998).

Many OM compounds (e.g. fulvic acid (FA) and humic acid (HA)) are heterogeneous macro-molecules containing a suite of aliphatic, aromatic, carboxylic, hydroxyl, phenolic and thiosulfate functional groups which determine OM characteristics such as solubility and bonding capabilities. One of the most important properties of NOM is its amphiphilic character, containing both hydrophilic and hydrophobic groups. OM research has typically involved use of well characterised, commercially available FA and HA (Wang et al., 2014a). These OM concentrates

or isolates, which include FA, HA, humin and lignite, vary substantially in solubility. For example, FA is defined as being soluble at all pH, HA as soluble at low pH and humin as being insoluble (Aiken et al., 1985). It is well known that FA and HA are able to transport metal ions in water over long distances (Lead et al., 1999; Lead and Wilkinson, 2006) by controlling the colloidal fraction (Joseph et al., 2013), and to promote metal accumulation though sedimentation. A close relationship exists between OM and mineralisation of U in many U deposits (Li et al., 2014), with wetland OM and plant roots having high capabilities to immobilise U (Li et al., 2015). A further characteristic is that OM (e.g. lignite and humate) has the capability to reduce U species (Nakashima et al., 1999; Nakashima et al., 1984; Nakashima et al., 1987; Sachs et al., 2006).

3.5.2. Uranium - organic matter bonding and stability constants

The precise mode of interaction of U with OM, however, remains elusive despite extensive, on-going studies (Bruggeman and Maes, 2010). Significant variation in the correlation of U and OM (organic carbon - OC unless otherwise stated) concentrations within natural samples have been reported. Strong ($R^2 = 0.74$ (reported as $R = 0.86$) (Meunier et al., 1989) and $R^2 = 0.85$ (Regenspurg et al., 2010)) and weak correlations ($R^2 = 0.52$ (Landais, 1996; Min et al., 2000)) have been reported between OM and U. Conversely, other studies have reported no statistical relationship between U and OC, either in sedimentary rocks (Kelepertsis, 1981) or groundwater (Yanase et al., 1995). Despite such variation, the occurrence of U within OM-rich environments has led to the postulation of a formal UO_2-OM bond. A few studies have indicated that formal U-OM bonding is possible under certain conditions (Alberic et al., 2000; Ray et al., 2011), and have suggested that more stable forms of bonding may be possible via FA and HA functional groups. In terms of the U oxidation state that might be favourable to OM bonding, Spirakis (1996) suggested that U(VI) was more favourable than U(IV), and drew this conclusion based on the greater degree of association of U(VI) and OM within sediments. This is in contrast to the results of Campbell et al. (2012), attained through x-ray analysis, who suggested that OM concentration in sediments results in a reduction of U(VI) to U(IV).

To further investigate U–OM bonding relationships, molecular investigations have been adopted by various researchers using both laboratory and modelling-based approaches. Research results have frequently provided evidence of UO_2-OM bonding (Haas and Northup, 2004). The outcomes of five studies are now introduced, the stability constants (log β) from each study are summarised in Table 3. Not only is there experimental evidence of binding to different OM components, but such bonds appear to be strong. A modelling approach to UO_2-OM binding was used by Lenhart et al. (2000). In assuming that bonding would occur to the 'carboxylic' functional group of either FA or HA, they applied data from ion exchange experiments to Schubert's modelling method. The FA and HA results were compared to 1:1 UO_2-citrate binding. Both FA and HA strongly bond to U(VI), with HA forming slightly stronger complexes but exhibiting greater pH dependence. A1:1 carboxyl acid group–uranyl bonding was indicated. Stability constants (log β) were calculated to be 6.996 ± 0.02 at $I = 0.1$ at pH 4 and 5. Stability constants for HA at pH 4 were $\log \beta = 8.39$ and at pH 5 were $\log \beta = 9.59$. For FA, log β showed less variation with pH, with $\log \beta = 7.31$ for pH 4 and 7.45 for pH 5. Lenhart et al. (2000) concluded that U will be complexed by NOM in environmentally relevant settings regardless of which modelling approach was used.

Kříbek and Podlaha (1980) examined the complexation of UO_2^{2+} ions with HA (extracted from peat) through titration experiments. They postulated that stronger binding would occur through phenolic groups as opposed to carboxylic and determined UO_2-HA stability constants to be $\log \beta_1 = 7.8 \pm 0.4$, independent of ionic strength. Their results compared well to other studies of metal-HA bonding. In an attempt to consider the effects of competition on the UO_2-HA bond, comparisons were undertaken with two uranyl carbonates, UO_2-CO_3^{2-} ($\log \beta = 16.2$) and UO_2-CO_3^{4-} ($\log \beta = 21.5$). The higher log β value for the uranyl-carbonates, implied that U was more strongly bonded to CO_3 than to HA, and was thus more likely to persist (Kříbek and Podlaha, 1980). Shanbhag and Choppin (1981) calculated $\log \beta_1$ (1:1) as 5.11 and $\log \beta_2$ (1:2) as 8.94 for the U(VI)-humate bond and concluded that such binding would occur via carboxylic acid functional groups. They added further that a U-OM bond would be able to compete with a carbonate complex until pH 8, at which point UO_2 would exclusively be complexed to CO_3^{2-} (see Fig. 3).

Table 3
Stability constants, Log β, for UO_2 – OM complexes.

Substance	Ratio	U(IV)/U(VI)	Log β	Conditions	Binding group	Ref
UO_2-cit	1:1	U(VI)	6.69 ± 0.003	pH 4, $I = 0.10$	cit	[1]
UO_2-cit	1:1	U(VI)	6.7 ± 0.03	pH 5, $I = 0.01$	cit	[1]
UO_2-HA	1:1	U(VI)	4.75 ± 0.08	pH 4, $I = 0.1$	carb	[1]
UO_2-HA	1:1	U(VI)	5.38 ± 0.08	pH 5, $I = 0.1$	carb	[1]
UO_2-FA	1:1	U(VI)	4.23 ± 0.04	pH 4, $I = 0.1$	carb	[1]
UO_2-FA	1:1	U(VI)	4.54 ± 0.06	pH 5, $I = 0.1$	carb	[1]
UO_2-HA	1:2	U(VI)	8.39 ± 0.08	pH 4, $I = 0.1$	carb	[1]
UO_2-HA	1:2	U(VI)	9.59 ± 0.06	pH 5, $I = 0.1$	carb	[1]
UO_2-FA	1:2	U(VI)	7.31 ± 0.06	pH 4, $I = 0.1$	carb	[1]
UO_2-FA	1:2	U(VI)	7.54 ± 0.06	pH 5, $I = 0.1$	carb	[1]
UO_2-HA	1:1	U(VI)	7.8 ± 0.4	pH 5 to 7, $I = 0.1$	carb and phe	[2]
UO_2-CO_3^{2-}	1:1	U(VI)	16.2	pH 5 to 7, $I = 0.1$	carb and phe	[2]
UO_2-CO_3^{4}	1:1	U(VI)	21.5	pH 5 to 7, $I = 0.1$	carb and phe	[2]
UO_2-Hu	1:1	U(VI)	5.11 ± 0.02	pH 4.04 ± 0.1*#	carb	[3]
UO_2-Hu	1:2	U(VI)	8.94 ± 0.10	pH 4.04 ± 0.1*#	carb	[3]
U(IV)-AHA	1:1	U(IV)	21.1 to 29.7	pH 6 to 9	phe	[4]
U(IV)$^-$BCHA	1:1	U(IV)	26.2 to 31.2	pH 6.9 to 8.9	phe	[4]
U(VI)-AHA	1:1	U(VI)	9.13	pH 8.4	phe	[4]
U(VI)-BCHA	1:1	U(VI)	4.42 to 8	pH 5.9 to 8.1	phe	[4]
$UO_2-HA_{(II)}$	1:2	U(VI)	6.7	pH 2 to 10	carb/phe	[5]
$UO_2^{2+}(OH)HA_{(I)}$	1:2	U(VI)	15.14	pH 2 to 10	carb/phe	[5]
$UO_2(CO_3)_2HA_{(I)}^{4-}$	1:1	U(VI)	24.47	pH 2 to 10	carb/phe	[5]

References: [1] (Lenhart et al., 2000); [2] (Kříbek and Podlaha, 1980); [3] (Shanbhag and Choppin, 1981); [4] (Warwick et al., 2005); [5] (Steudtner et al., 2011).
OM abbreviations: Aldrich humic acid (AHA); boom-clay humic acid (BCHA); fulvic acid (FA); humate (Hu); humic acid (HA).
Functional group abbreviations: carb = carboxylic acid; cit = citrate group; phe = phenolic acid.
*no notable effect on temperature between 275 and 307 K.
#U would be complexed to CO_3 above pH 8.

Whilst the above studies considered the U(VI) bonding to OM, Warwick et al. (2005) examined the possibilities of both U(IV) and U(VI) oxidation states binding with two types of HA, an Aldrich HA (AHA) and a boom-clay HA (BCHA), under carbonate free conditions. The stoichiometry for all binding scenarios was more consistent with a 1:1 U:HA ratio than a 1:2. They reported an increase in log β values of U(IV)-AHA with an increase in pH from 6 to 9. The stability constants for U(IV)-AHA were log β = 21.1 to 29.7 for pH 6.4 to 8.6 and increased slightly for U(IV)-BCHA, log β = 26.2 to 31.2 for pH 6.9 to 8.9. They also reported stability constants for U(VI)-AHA as log β = 9.13 for pH 8.4 and for U(VI)-BCHA as log β = 4.42 to 8 for pH 5.9 to 8.1. The values reported by Warwick et al. (2005) for U(VI) are consistent with the U(VI)-HA log β studies of Lenhart et al. (2000), Kříbek and Podlaha (1980) and Shanbhag and Choppin (1981). Overall, they suggest that U(VI)-HA bonds are relatively strong. We can also infer from the Warwick et al. study that the U(IV)-HA bond appears to be stronger in contrast with earlier interpretations of Spirakis (1996). One area of continuing uncertainty is the functional OM group with which U is bonded. We can, however, assume with higher probability that carboxylic or phenolic bonding sites are the likely bonding moieties for U with HA.

As summarised in Table 3, the U(VI) bonding (as log β) to various OM (FA, HA or citrate; phenolic or carboxyl) were similar and averaged at U(VI)-OM = 6.9 ± 1.8. Although investigated by fewer studies, the respective value for U(IV) was three times higher at 23.7 ± 3.6. The log β value obtained for OM-U(VI)-CO_3 was 24.47, which was higher than U(VI)-CO_3 on its own (18.8 ± 3), these figures being derived within separate studies.

Whereas the studies reported above investigate bond formation in a laboratory context, other more theoretical perspectives suggest bond instability. Over geological timeframes various changes in the NOM hosting U are likely to occur, including diagenetic alteration through oxidation, biodegradation, aromatisation, radiolysis and thermal maturation (Nakashima, 1992). The potential change in the molecular environment of the organic geochemistry introduces uncertainty into the enduring stability of UO_2-OM bonding sites. As OM matures, a range of functional groups may dissociate, through, for instance, microbial activity, potentially leading to the release of UO_2. A further cause of U-OM degradation is from the decay of U itself. Through radioactive decay, U radiolysis of adjacent OM molecules may occur resulting in bond degradation (Cortial et al., 1990; Drennan and Robb, 2006) with damage to surrounding material often observed in the form of halos (Gentry et al., 1976; Leventhal et al., 1987).

3.5.3. U - OM sorption and dissolution

There is little information on the solubility of U-OM complexes within the literature (Luo and Gu, 2008; Manaka et al., 2008; Tinnacher et al., 2013), as more attention has been directed towards U-OM sorption and dissolution. A study by Manaka et al. (2008) investigated varying U concentrations along a stream. Lower concentrations of U were attributed to sorption within certain stream zones, with the loss greatest in regions of highest organic debris. Not only was U likely to absorb onto HA, but also onto detrital decomposing leaves. Higher U concentrations found downstream implied that sorption might be temporary, as disturbances to OM, such as increased flow rates, could re-suspend particulate U.

The presence of OM may also mediate uptake of U on mineral surfaces. A study by Tinnacher et al. (2013) examined different rates of FA, U, and U-FA sorption onto silica sand. The study showed that maximum sorption varied with pH and concentration of U or OM. When U(VI) (10^{-8} M) was added to silica it was near fully absorbed at pH 6.5. In contrast, maximum sorption of FA (10^{-8} M) to silica, approximately 50% of the concentration, occurred at pH 4.5. The U(VI)-FA (U = 10^{-7} M) compound showed the highest absorption at the lowest FA concentration (10^{-8} M), where 50% was absorbed at pH 6. When the FA concentration was then increased to 10^{-5} M, only 20% absorption occurred over a pH range of 4.5 to 8. Sorption of U(VI) onto silica was therefore retarded both by the presence of FA and by increasing concentration of FA. The change in sorption was also found to be critically dependent on metal speciation and the relative concentration of metal, organic ligands and mineral surfaces.

Luo and Gu (2008) examined the re-suspension of U(IV) and U(VI) from contaminated sediments and the influence of HA and FA. Under anaerobic conditions they determined that HA was more effective than FA in causing the dissolution and mobilisation of U(IV). This was attributed to the greater solubility of FA at higher pH and electron donation under anaerobic conditions. It was further concluded that carbonates were effective in dissolving U(VI) but not U(IV) species.

4. Relationships among U, organic matter and inorganic ions

Previous sections of this review have synthesised research investigating the relationship between U and complexing ions, U and Fe and U and OM. In recognition of the concomitant presence of U inorganic and organic complexing ions (OM) and Fe within many geological settings, this section examines potential interactions in multi-component systems. In doing so, it is recognised that U stability and mobility is influenced by complex interactions between these components. Attention is directed towards the relationship between U, OM and either carbonates, vanadates or ferrous/ferric, with the understanding that in these multi-component systems a range of competitive effects will determine binding to uranyl ions, their mobility, and/or sorption onto solid phases (De Windt et al., 2003; Zielinski and Meier, 1988). The second part of this section then examines multi-component laboratory-based investigations that provide the basis through which modelling-based investigations seek to predict outcomes in terms of U solubility, transport and precipitation. The benefits of modelling can be seen in terms of helping to understand outcomes beyond laboratory timescales.

Where present in sufficient concentrations, CO_3^{2-} will complex with UO_2^{2+} by out-competing other moieties, including OM, particularly at intermediate to high pH (Fig. 3b). For example, CO_3^{2-} may react with an existing uranyl–humate leading to the formation of a uranyl carbonate complex, as postulated by Zielinski and Meier (1988) in Eq. (2) for a 1:1 reaction and in Eq. (3) for a 1:2 reaction.

$$UO_2(Hu) + 2CO_3{}^{2-} \leftrightarrows 2(Hu)2^- + UO_2(CO_3)_2{}^{2-} \quad \text{(Eq. 2)}$$

$$UO_2(Hu)_2 + 2CO_3{}^{2-} \leftrightarrows 2(Hu)^- + UO_2(CO_3)_2{}^{2-} \quad \text{(Eq. 3)}$$

An alternative outcome to that presented in Eqs. (2) and (3) is the formation of a hybrid uranyl humic carbonate. Steudtner et al. (2011) determined stability constants for the U(VI)-OM bond using UO_2^{2+} compounds with OH^-, CO_3^{2-} and HA species. In the case of $UO_2HA_{(II)}$ their results of log β = −6.7 were similar to those in Section 3.5.2 (see also Table 3). For $UO_2^{2+}(OH)HA_{(I)}$, log β = 15.14 and for $UO_2(CO_3)_2HA^{4-}_{(II)}$, log β = 24.47. They concluded that the strongest and most likely bonding combination was 1:2 $UO_2(CO_3)$HA as either 1:1 or 1:2 HA complexes. Accordingly, this ternary complex could be important in the mobility of U as a soluble complex, particularly at circumneutral to alkaline pH (see also Fig. 2b).

The relationship of U, OM and V provides an example multi-component system, as whilst the interaction of U-V and OM-V has been well documented, few studies have examined the components collectively (Tokunaga et al., 2009; Tokunaga et al., 2012). Major U–V deposits are common globally, with prominent examples reported in the Colorado Plateau Utah (Fishman et al., 1985; Gustafson, 1949; Hansley and Spirakis, 1992; Hostetler and Garrels, 1962; Meunier et al., 1987; Miao et al., 2013; Shawe, 2011) and in Western Australia (e.g. Mulga Rock OM deposit; (Douglas et al., 2011)). Such co-occurrences of U and V are not unsurprising due to their similar aqueous geochemistry (Levy et al., 1994; Wood, 1996) and affinity for OM–rich environments. Vanadium, in particular, is known to bond strongly to OM, especially to carboxyl sites, which explains high V occurrences in crude oil, bitumen and lignites (Mossman, 1999; Pommer, 1957). Vanadium-OM bonding is

also attributed to V's variable coordination numbers (from 4 to 8) and flexible 'entatic state', allowing it to bond to both biological proteins and heterogeneous NOM (Jouffret et al., 2010; Kanamori and Tsuge, 2012). In addition to bonding, OM can reduce V(V) to V(IV), and possibly even to V(III) (Pommer, 1957; Wood, 1996), and in solution, dissolved V-OM is likely to be reduced and complexed (Breit and Wanty, 1991), particularly as the V(III) coordination is more suited to OM bonding (Kanamori and Tsuge, 2012).

Aside from pH, the presence of OM is highly influential in sorption of U(VI) compounds onto iron oxides. Several studies examining U, OM and Fe in a multi-component system, have shown that UO_2 absorption onto various Fe minerals (i.e. ferrihydrite, hematite) may be enhanced in the presence of OM and at low pH (Lenhart and Honeyman, 1999; Payne et al., 1996). In a further study by Zhao et al. (2012), the presence of OM appeared to influence the pH range at which sorption was most likely to occur. Zhao et al. (2012) demonstrated this by showing that in the presence of HA/FA the sorption of U(VI) onto hematite increased below pH 6.0, but was retarded above pH 6.0. The rate of U sorption was also decreased with an increase in the concentration of OM (as HA). Guo et al. (2009), investigated a multi-component relationship that involved goethite demonstrating that maximum sorption of UO_2 onto goethite occurred above pH 5, which was found to be independent of ionic strength. In contrast the addition of FA (20 mg L^{-1}) appeared to have little effect on U(VI) sorption to goethite. In the same study by Guo et al. (2009), U(VI) sorption was investigated onto goethite in the presence of PO_4^{3-} and CO_3^{2-}. Where, U sorption onto goethite was promoted by high PO_4^{3-} (6×10^{-4} mL^{-1}) concentration, especially between pH 2.3 and 4.5. They found that the effect of P_{CO2} decreased the level of sorption with greatest effect at pH > 8.2, indicating that CO_3^{2-} was strongly influential in preventing sorption of U to goethite at high pH. In a study by Echevarria et al. (2001), soil pH (4–9) had a greater influence on sorption ratios for UO_2^{2+} than either soil OM or clay content. Furthermore, the amount of sorption of UO_2^{2+} on soil decreased with increasing pH, thereby enhancing the potential for U mobility (Echevarria et al., 2001).

Other components (e.g. As, Cu, Pb, Zn) in organic sediments may influence U sorption through competition for sorption sites. For example, U may absorb readily to sediments coated with Fe-minerals, such as magnetite (Kukkadapu et al., 2010), but the presence of other metals, such as Se, V, Cr, As, Cu and Zn, may affect U sorption (Qafoku et al., 2014). The competition of other species on U sorption has received relatively little attention in the literature, however this may be important for understanding U migration from contaminated sites, particularly when implementing control strategies (Mouser et al., 2015).

The comparative solubilities of U-complexes discussed in Section 3 are summarised in Fig. 5. The most influential factors affecting U-solubility are pH, Eh, oxidation state, OM, redox (including microbial) and complexing ions. The pH threshold for U solubility is around pH 6, above which U becomes increasingly soluble. Eh and microbial redox affect U mobility by altering the U oxidation state, with U(IV) more insoluble. In the U(VI) form, solubility is largely determined by organic or inorganic complexing ions and concentration. At low OM concentration, U solubility is promoted, whereas at high concentration OM may immobilise U. OM type also affects U solubility with fulvic acids more likely to prevent U dissolution and sorption, e.g. onto iron mineral surfaces, than humic acids. Of all the inorganic ligands, U carbonates are the most soluble, particularly when compared to other ions such as SiO_2^{4+} and PO_4^{3-}.

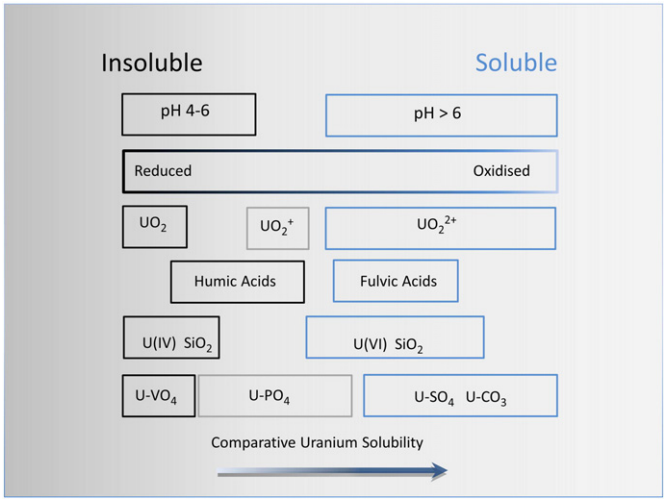


Fig. 5. Conceptualisation of the factors affecting U solubility.

4.1. Reactive transport and surface complexation modelling

Thus far this review has identified how the mobility and stability of U is influenced by factors including pH, Eh, redox, ion availability (e.g. CO_3^{2-} or PO_4^{3-}), OM constituents, microbes, EPS and sorption potential onto surrounding geochemistry. To a significant degree, data are experimentally derived within controlled and constrained environments. This contrasts with the complexity of the natural environment where the fate and transport of U must be considered within the context of hydrological mixing, interactions at various solid-water interfaces and within dynamic environments, such as roll front deposits (Jardine et al., 2002). Whereas laboratory-based experiments tend to be linear, steady state (isotherm) or 2-D representations of surface water flow, the migration of (U) pollution plumes is likely 3-D, thus creating unpredictability (Yabusaki et al., 2008). Furthermore, U migration pathways may operate beyond realistic laboratory timeframes, with knowledge required for 10^2 to 10^6 years post hence (Bain et al., 2001; Bea et al., 2013; Dittrich and Reimus, 2015; Gurban et al., 2003; Santos and Ladeira, 2011). To address some of the issues involved in predicting U fate and behaviour, and to compliment field-based analysis, various environmental models have been developed (e.g. Kantar (2007)). The benefits of modelling can be seen in terms of enabling scientists to draw together knowledge of geological processes (Section 2) and geochemical processes (Section 3). Alternatively, modelling can be applied to specific situations, such as radioactive material spillages, active mine tailings or the assessment of risk of contaminant migration following a mine closure (Gómez et al., 2006; Gurban et al., 2003).

Two modelling approaches exist: isotherm (K_d), which is incorporated into surface complexation models (SCM), and reactive transport models (RTM), which relate to the system's hydrodynamics. Isotherm (K_d) models have been applied to predict species outcomes at equilibrium under a steady state of pH and ionic strength (I). SCMs interrogate sorption effects quantitatively, such as U onto Fe-oxides, and co-sorption effects, such as of Fe-oxides onto other surfaces (e.g. silica) and OM onto U (Waite et al., 2000; Waite et al., 1994). Reactive transport models predict the baseload of hydrologic transportation based on advective-dispersive equations.

Within the modelling context, one major question is the extent to which soluble U, either precipitates or adsorbs to minerals surfaces (Dittrich and Reimus, 2015; Kim et al., 2015; Zhang et al., 2011). Depending on how such processes are understood and weighted, multiple outcomes might be attained, in respect to spatial and temporal U migration (Bain et al., 2001). In the study of De Windt et al. (2003), which was concerned with the migration of radioactive pollutants, the sorption of U to Fe-oxides (goethite and hydrous ferric oxide) was investigated through a range of RTM models, including CASTEM (CEA, 1999), CHEMTRAP (Lucille et al., 2000), HYTEC (Salignac, 1998) and PHREEQC (Parkhurst, 1995; Parkhurst and Appelo, 1999). The results obtained from each model were considered to be in good agreement. In contrast,

however, exists with a comparative model based study undertaken by Yabusaki et al. (2008). The focus for this study was a U plume at the Hanford site 300 Area, US, with Yabusaki et al. (2008) concluding that discrepancies existed between the models. Differences were detected in terms of the time frame over which U would migrate, with some models predicting a higher degree of sorption onto available sediments. This reinforces the realisation that whilst SCMs are increasingly replacing original isotherm models in RTMs, and SCMs are undergoing continuous development to include important molecular interactions (Kim et al., 2015), on-going attention is required to improve the accuracy of both SCMs and RTMs in the prediction of U migration. Such work must seek to address underlying debates about model parameters and associated assumptions (e.g. competing hypothesis concerning electrical double layer exist (Kantar, 2007)).

As increased industry and academic research has been directed towards OM-rich environments because of their potential to concentrate economic U, the heterogeneous nature of OM has been recognised. Whilst OM may have previously been excluded from modelling because of an absence of fundamental data on reactivity and complexation characteristics, its importance has led to its inclusion, though questions of parameter accuracy also arise (Fox et al., 2012). Bryan et al. (2012), for example, state that whilst the characterisation of OM within environmental models has improved, further improvements are nevertheless required. Inherent within the latter is the realisation that OM is not only heterogeneous between deposits, but that it is also spatially variable within an OM-U deposit. Hence, modelling must account for the OM variability (Bryan et al., 2012; Davis et al., 2004; Kantar, 2007; Tipping, 1998). Kantar (2007) raises further considerations by acknowledging that the role of key aspects of OM remain underexplored (e.g. extracellular polysaccharides), thus reconfirming the need for laboratory-based research and modelling-based prediction to advance together. An additional consideration raised by Kantar (2007) is whether electrostatic forces and their role in shaping the movement of particles/colloids should be included.

Even where site specific OM is better characterised, the potential for modelling inaccuracies remains because the impact of OM on U may be difficult to determine and produce a variety of outcomes, such as enhancement or retardation of surface sorption (Dittrich and Reimus, 2015; Zhang et al., 2011). By way of example, where OM bonds with U, then OM play an active role in preventing U from adsorbing to mineral surfaces (e.g. goethite). Alternatively, OM may be responsible for U entrapment without U(VI) reduction. Ortaboy and Atun (2014) used models to predict U-sorption to OM, where the sorption was successfully predicted by the Dubinin–Radushkevich, Dushkand and Langmuir isotherm models, but the Freundlich isotherm model performed less well against experimental data. Bonding and sorption processes may both occur within the natural environment, thus necessitating careful consideration of the OM-U interactions that underpin modelling.

Another aspect of OM which has been identified as a key influence shaping U mobility and stability is microbial activity (Stewart et al., 2011). A challenge for existing environmental models is therefore to integrate emerging knowledge about the impact of microbes on U mobility and stability (Law et al., 2011). Two considerations are critical. First, as documented within this review, both chemical and microbial influences may determine the fate of U within OM-rich settings (Hunter et al., 1998; Istok et al., 2010; Scheibe et al., 2006; Stewart et al., 2011). What is less well considered is the time frame over which both operate. Similarly to OM, the inclusion of microbial activity raises complex questions about the weighting that models give to different processes over time (Campbell et al., 2015).

Second, it must be recognised that different microbial populations exist within OM (Fang et al., 2011) with the potential to produce a variety of outcomes. For example, laboratory-based research increasingly recognises how, depending on the microbial group, microbes can reduce U(VI) into either uraninite or into a biogenic non-crystalline U(IV) (Alessi et al., 2014b). The implications for the fate of U are substantial as the latter is considered more unstable, and may thus more readily revert back to the more soluble U(VI) oxidation state. In ways that strengthen the importance of linking laboratory-based research and environmental modelling, Long et al. (2015) acknowledge the need for models to more carefully consider post-bioreduction phases. Fang et al. (2011) has further shown that a constraint-based model approach coupled with RTM was useful in predicting the metabolic pathways of bacteria species for each metal in respect to their genome. Thus in order to proceed with modelling enquiries, the capability and rate of microbial metal processing requires further investigation, with evidence then integrated into models to explain U migration.

5. Conclusions

The mobility/stability of U is influenced by a suite of inorganic, organic and microbial processes often operating in parallel. The net outcome of such processes determines whether U mobility is retarded in such a way that U can become stabilised within deposits. Understanding how these processes operate has importance throughout the U life-cycle; from exploration and mining, to depositing spent nuclear fuel and monitoring U within surface or groundwater.

Inorganic influences on U mobility are two-fold: first, in controlling U oxidation state, where U(VI) is more mobile than the reduced U(IV); and second, in the formation of inorganic UO_2^{2+} species. In the case of the latter, inorganic UO_2 compounds vary in solubility according to species and the Eh and pH conditions, for example, UO_2CO_3 compounds have the highest degree of solubility at pH > 6. Where present, competition for the UO_2^{2+} ion exists among the ionic groups, CO_3^{2-}, OH^- and PO_4^{3-}, and to a lesser extent SiO_4^{4+}, SO_4^{2-} and VO_4^{3-} species. Depending on which U species are formed dictates the fate of U and whether U is likely to migrate, adsorb or precipitate within the environment.

The behaviour of U can also be affected by other processes. Iron, for example (as oxides or sulphides), has two main influences on U influencing both redox state and sorption. Extensive research into the influence of various Fe oxides on U has shown variation in reaction or sorption behaviour depending on which Fe oxide is used (e.g. hematite, goethite, magnetite or ferrihydrite) with sorption further mediated by the presence of OM. This variation in many cases could be explained by the surface, solubility and oxidation state (Fe(II)/Fe(III)) properties of each of the iron oxides. Importantly, Fe(II) compounds (e.g. FeS) have the potential to reduce the mobile U(VI) to insoluble U(IV) minerals.

The addition of OM to inorganic paradigms related to U solubility and mineral formation is less well understood, but its impact is profound. At even low concentrations, soluble OM can prevent U sorption and lead to increased mobility. Alternatively, where solid OM is present, U mobility may be reduced through complexation and mineral formation. Under aqueous conditions, OM can act as a ligand and compete with inorganic ions for U. Sorption of U may also be retarded in these conditions, though this largely depends on OM type and nature of surfaces (e.g. Fe-Oxide). Thus at low OM concentrations, U mobility may be more significant than previously thought. The impact of U on OM, at percent OM concentrations, however, may be quite different. Here OM may act as a trap for mobile aqueous U enabling deposit formation. There is more limited evidence, however, as to whether OM may further immobilises U though reduction to U(IV). Where U reduction has occurred within OM, it may have resulted via a series of biotic and abiotic pathways. Understanding how natural OM influences U and other metals in the environment has been constrained by the heterogeneity across OM types and within the macromolecules. One approach adopted for purposes of modelling, has been to classify OM according to a series of functional groups (e.g. carboxyl, phenolic) for each OM type (e.g. fulvic acid, humic acid), as a surrogate for their reactivity towards U.

Studies that have examined multi-component systems have focussed on UO_2, Fe and OM with and without the presence of CO_3^{2-}. In most situations above pH 6 carbonates tend to dominate, with U-OM bonding mostly occurring below pH 5. Very few studies have included U-PO_4 with OM, yet the relationship might be important at low pH. Studies are also lacking in the relationship of either U-SO_4 or U-VO_4 with OM, both of which could be significant in the absence of CO_3^{2-}. Whilst there is a common association of V with U–OM deposits, with U–V inorganic minerals commonly formed, few studies have investigated U-V-OM relationships in depth to establish whether V has any influence on U mobility or stability in OM-rich systems.

The occurrence and formation of U-colloids, within OM and the impact of U mobility is one that is worthy of further investigation. Colloids and nanoparticles, are potentially highly mobile in the environment. This has particular importance because in terms of the oxidation state, inducing reduction may therefore not render U less mobile, where U(IV) colloids are formed. Moreover, surface coating by OM could further enhance transport though aquifers.

Microbial reduction of U(VI) is of considerable interest as a mechanism for controlling U mobility in contaminated sediments. Equally, these microbial processes hold relevance for natural settings. Within microbial communities there are a plethora of groups with metal-reducing capabilities. These capabilities require further investigation to identify specific processes involved in U capture and reduction in OM-rich systems.

Predicting U mobility in the environment through SCM and RTM modelling can realistically be determined both spatially and temporally. In making viable predictions, effects such as competition between anions, and the effects of OM and microbes on U geochemistry should be incorporated.

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