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BINDING, SENSING AND SYNTHESIZING BIO-TRANSFORMATIONS OF URANIUM

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ABSTRACT

Uranium bio-transformations are the many and varying types of interactions that microbes can have with uranium encountered in their environment. In this review, bio-transformations, including reduction, oxidation, respiration, sorption, mineralization, accumulation, precipitation, biomarkers, and sensors are defined and discussed. Consensus and divergences are noted in bioavailability, mechanism of uranium reduction, environment, metabolism and the type of organism. The breadth of organisms with characterized bio-trans formations is also cataloged and discussed. We further debate if uranium biotransformations provide bio-protection or bio-benefit to the microbe and highlight the need for more work in the field to understand if microbes use uranium reduction for energy gain and growth, as having the ability is separate from exercising it. The presentation centers on the fundamental drivers for these processes with an additional exposition of the essential contribution of inorganic chemistry techniques to the molecular characterization of these biological processes.

Key Words: Uranium, Reduction, Bio-Sorption, Proteobacteria

I INTRODUCTION

Metals are an essential part of life comprising cofactors, nutrients, chlorophyll, electron acceptors and donors, color creators and more. Although man has used metals extensively since copper was discovered in 9000 B.C.E., we are just beginning to appreciate the ability of biology to manipulate metals [1] . Uranium is not considered an essential metal for biological processes, but has become an essential part of lifestyle in the 20th century through the development of nuclear technologies from weapons to clean energy to medicine. Uranium is the largest stable element found on the planet Earth. While radioactive, the half-life is 4.5 billion years, meaning that it decays very slowly. Uranium is found naturally throughout the Earth's crust with an average of 2.7 mg of uranium per kg of crust. Although uranium concentrations are much higher in naturally-occurring uranium deposits, some of which are mined for uranium [2] [3] , in the Earth's crust, uranium is found mostly in mineral complexes [4] .

Despite the low-level natural abundance of uranium in soils, human activities have introduced dramatically high concentrations of uranium to water and soils near uranium mines, near other metal mines that also have high uranium content, near nuclear weapons manufacturing and testing sites, and near nuclear power plants—creating

high concentrations of uranium in formerly pristine sites [5] . The vast majority of the human-introduced uranium has been a relatively recent activity. It started with the atomic age beginning in the 1930's and escalated after the conclusion of World War II into the Cold War. Still today, more countries are attempting to make nuclear weapons or use nuclear power. These contaminated areas sometimes represent a significant global threat to human and environmental health and safety, demanding a need for remediation or immobilization by non-intrusive methods. Although the contaminating uranium is often depleted in the fissile Uranium and, therefore, does not present a severe radiological risk, but Uranium is still a highly toxic heavy metal [6] . Uranium poisoning affects humans by oxidatively damaging cells causing non-malignant respiratory disease and nephrotoxicity [7] . For the eco-systems at these sites, uranium pre-sents a significant challenge. Although uranium can be adsorbed to roots and be taken up by plants, processes that were initially considered possible remediation strategies, the toxic metal ultimately harms the plant [8] [9] . Similar damage occurs to microbes in that uranium causes oxidative damage to the cell and the DNA. However, despite the high toxicity and potential radiation damage from uranium, some naturally-occurring microbial communities have the ability to survive, and even thrive, in highly contaminated uranium conditions. These capacities yield the desired non-intrusive remediation or immobilization methods [10] [11] .

The ability to persist in a uranium contaminated environment is achieved through a number of different types of bio-transformations, typically chemical transformations of the metal carried out by a microbe. Microbes have been observed reducing, oxidizing, respiring, adsorbing, mineralizing, accumulating or precipitating uranium in the environment [12] . These interactions have been investigated as remediation strategies and in some cases characterized molecularly as unique chemical transformations and electron flow pathways. Microbes of all shapes and sizes have been found to have different interactions with uranium from Proteobacteria to fungi [13] [14] . The widespread nature of the bio- transformations of uranium both geographically and by various microbial families brings into question whether the bio-transformations are biologically or chemically driven? In other words, is any organism in the right redox environment capable of transforming uranium and are there biological advantages to the organisms carrying out these bio-transformations? An open question for researchers in the field has been whether these transformations are detoxification, resistance or just accidents of chemistry?

Previous reviews have discussed uranium reduction, uranium bioremediation methods [15], uranium geochemistry, mineralization and groundwater transport [16]. While all substantial and important reviews, the previous work has focused only on the most well-known organisms and do not consider the drivers of these processes or the biological benefit to the microbe beyond mentions of possible detoxification. In this paper, we expand beyond the more commonly presented reduction and remediation to provide a current list of reported/characterized uranium bio-transformations.

II BINDING, SENSING AND SYNTHESIZING BIO-TRANSFORMATIONS OF URANIUM

2.1 Sorption

Bio-sorption of uranium is the process where the uranium is immobilized on the outer membrane or extra polymeric substance of the microbe. This can follow a redox event, but can also be redox independent. It can likewise sometimes rely on charge, but can also be due to electrostatics since uranium is "sticky." Sorption is one of the more commonly referenced bio-transformations in the literature because it is a possible remediation strategy. Some cells can adsorb uranium up to nearly half their cell weight, but this appears to be a passive, non-enzymatically driven process.

Examples of microbes carrying out biosorption include the fungus Talaromyces emersonii. At pH 5, the fungus had a biosorption capacity of 280 mg U per gram of dry cell weight. With maximal biosorption of 0.44 g U per gram of dry cell weight at pH 4.6, the Actinomycetes bacterium Streptomyces longwoodensis efficiently removes uranium from liquid samples. The amount was dependent on several factors including cell phosphorous content, pH, uranium concentration, and cell-cycle stage. Bacillus isolates from Saxony were able to take up uranium efficiently in the 10 - 200 mM range and the metal was found adsorbed to the S-layer proteins and cell surface. In a surprising finding, Thorgensen and co-workers identified an S-layer protein complex in Pelosinus sp. Strain UFO1 that binds U(VI), but does not reduce it. Diverse organisms such as At. ferrooxidans and Acidovorax facilis are also reported to adsorb uranium. Even non-uranium-reducers or organisms not found in uranium contaminated environments, such as Saccharomyces cerevisiae and Staphylococcus aureus LZ-01, can adsorb uranium efficiently. The chemical species of the adsorbed uranium varies and reflects the state of uranium in the environment. Uranium is often tightly bound, complexing to phosphoryl, carbonate or occasionally nitryl ligands and side chains. Therefore biosorption can be an attractive method for bio-remediation.

2.2 Accumulation

Accumulation can sometimes be referred to interchangeably with bio-sorption. However, sorption and accumulation are generally differentiated by the location of the bio-transformed uranium relative to the cell. Accumulated uranium is located within the cell, either in the periplasm or cytoplasm, but must have traversed at least one membrane. Like biosorption, Cellulomonas and fungi have been shown to accumulate impressive amounts of uranium. As discussed in the reduction section, the mechanism of uranium entry into the cell is unknown. It is also not well-characterized how the accumulation of uranium impacts cell growth and survivability, but the suggestion is that it is detrimental or neutral at best, but does not apparently benefit the cell.

2.3. Mineralization

Bio-mineralization is also more generally defined as the formation of U(IV) species, which is insoluble and called the mineral uraninite, UO_2. However, this is the end product of bio-reduction, so the terms are sometimes

used interchangeably. Bio-mineralization can also be more specifically defined as an active enzymatically driven process where the uranium is transformed to insoluble non- oxide mineral, usually metal phosphates. The mechanism of bio-mineralization has been well-characterized in the γ-Proteobacteria Serratia sp. Uranium is trapped on the surface of the cell or in the extracellular matrix on material like EPS, extracellular polymeric substances Meanwhile, the enzyme phosphatase, that can be found on the outer membrane and can also be excreted into the extracellular matrix, creates inorganic phosphate by hydrolyzing the phosphate from soluble phosphate organic compounds or minerals. The surface-complexed uranium, phosphate and often calcium react forming immobilized minerals. In Serratia this is seen under fermentative growth and different minerals may be produced under phosphate limited conditions.

In addition to Serratia, the C. crescentus bio-mineralization mechanism is also well studied and the specific periplasmic phosphatase releasing phosphate, PhoY, has been determined. Citrobacter sp. also bio-mineralizes uranium on the cell surface forming phosphate minerals with phosphate, while ammonium addition to the mineral produces an even more insoluble form. Arthrobacter sp. and Microbacterium oxydans from mine tailing sites were also found to produce uranium phosphate minerals, confirmed by High Resolution Transmission Electron Microscopy.

Uranium can be mineralized into a variety of uranyl-phosphates by active microbes. The term bio-precipitation is also used when the specific process is unknown, but solid uranium particles are observed such as in a batch community system or environmental field site. A well- known bio-precipitation is mediated by Citrobacter sp., which forms slightly yellow uranyl phosphates.

2.4. Bio-Markers of Uranium Bio-Transformations

Bio-markers are small molecules, genes, proteins or even isotope fractionation ratios that consistently correspond with a biologically-driven process. Isotope fractionation is the process where microbes preferentially consume a specific isotope of an element creating an enrichment of the preferred isotope in the end product that differs from the natural abundances of the isotopes. The enrichment is usually a constant ratio. If isotope fractionation values are known for certain biologically-driven processes and that fractionation value is found in samples, it is strong evidence that the process occurred biologically even if the bacteria responsible are no longer present, such as in deep cores from early Earth eras.

Bio-makers have been used to detect uranium biotransformation that took place millions of years in the past. Uranium reduction does have a known, although difficult to measure isotope fractionation value that actually enriches the heavy isotope. Rademacher and coauthors compared the isotope fractionation for uranium reduction from an abiotic process with zero valent iron particles and bioreduction by Geobacter or Anaeromyxobacter. They found that the biotic process produced a very similar negative epsilon (enrichment factor) value for both bacteria, while the abiotic iron process resulted in the same ratio as natural abundance. Dang et al. also compared biotic and abiotic pathways and came to the same conclusion, but with the addition that certain minerals such as mixtures of iron and manganese have an isotope preference for the lighter isotope, U-235. The

Bernier-Latmani group has also measured a uranium signature with preference for the heavy isotope and has used this signature to detect microbial activity in rocks from multiple ages of Earth history including Archean and Cretaceous. A proposed biomarker for Geobacter is the amount of the genus specific GltA protein. Wilkins et al. showed that there was a strong correlation between copy numbers of the protein versus uranium reduction activity during stimulated bioremediation. With modern technology, ancient and current uranium bio-transformations are detectable.

2.5. Bio-Sensors

Knowing the nature of the chemical interaction between microbes and uranium has enabled the creation of bio-sensors for uranium in the environment that have taken a variety of forms. Bacterial community composition has even been used as a geo-sensor to predict the location of uranium contamination. Antibodies to certain uranium chemical species have also been developed as an environmental biosensor.

UO2-selective DNA-zymes, which are engineered pieces of DNA designed to specifically bind the uranyl ion and then cleave a fluorescent molecule containing DNA arm, releasing the molecule which emits fluorescence. Quenching the fluorescence with a 2D layer of molybdenum disulfide nanosheets allows the decrease in fluorescence to be a readout for U(VI) concentration.

C. crescentus has been used as a whole cell uranium biosensor by engineering the organism to produce fluorescence when excited with UV light and when its environment contains uranium. As a fluorescent biosensor, this bacterium has a detection limit in the nanomolar range. Bio-sensing presents an in situ method for uranium detection in the environment.

2.6. Biofilm/Biobarrier

Bacterial biofilms are sessile tight assemblages of a microbial population that create micro-environments or niches that may be different than the surrounding environment. Biofilms have shown enhanced uranium sequestration and immobilization in single organism and multi-organism biofilms. Biofilms of strains of iron-reducing Shewanella species were found to immobilize uranium efficiently, and Shewanella extracellular polymeric substances played a very large role in that immobilization with the assistance of reduction by the outer-membrane cytochromes. However, reduction capability was dependent on biofilm architecture and the reactor used to measure that structure. Examination of Geobacter biofilms saw increased uranium resistance up to 5 mM uranium and better immobilization compared with planktonically grown cultures; the conductive pili and cytochromes were major contributors to the biofilms enhanced resistance. Desulfovibrio biofilms routinely formed nanocrystalline U(IV) over other crystal types formed by planktonic cultures.

Looking at community-scale biofilms, rhizosphere communities growing on iron-plaques in the DOE Savanah River Site were also found to have enhanced uranium reduction and immobilization. Stemming from the increased immobilization with biofilms, some remediation strategies include biofilms as a form of bio-barrier to trap the uranium or are working to develop the biofilms to deploy in permeable reactive barriers. New laser-based fluorescence techniques have been employed to determine the chemical species of uranium in the biofilm environment. Biofilms characteristically have increased interactions between the microbes which results in altered or enhanced interactions with uranium.

2.7. Nano-Particle Synthesis, Nano-Wires

In the bacterial produced nano-realm, nano wires, fibers and particles have been described with reduced uranium. Nano-wires/fibers of meta-schoe- pite mineral polycrystalline chains were produced by S. oneidensis MR-1 during uranium reduction. Another reduction reaction could reduce these nanowires to nanoparticles. Cytochromes were found to be necessary for nanoparticle U(IV) formation by Shewanella. Structural characterization of Shewanella biogenic uraninite nanoparticles suggested that the synthesis pathway was thermodynamically driven. The long conductive pili of Geobacter with and without cytochromes have also been called nanowires because of their ability to transmit electrons. The bio-produced nanomaterials have benefit to the cells and could be used by humans for remediation or other electronic applications.

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