

Interactions of U(VI) with archaea: what is different than with bacteria?

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Archaea, in contrast to the diverse and dense bacterial populations, occur in uranium mining wastes in low numbers and belong mostly to particular crenarchaeal groups, some of them not yet cultured [1,2]. On the example of the thermoacidophilic crenarchaeon *Sulfolobus acidocaldarius*, indigenous for many uranium contaminated wastes [3,4], we demonstrate that archaea tolerate substantially lower concentrations of U(VI) than bacteria and that they interact with this radionuclide in a significantly different way. One of the reasons for this behaviour is the unusual cell wall structure of the representatives of *Crenarchaeota* which is restricted to a single proteinaceous surface layer (S-layer), that is in contrary to the complex, rather thick, and rich on metal-binding ligands cell wall structure of bacteria. Due to the extreme acidic and mechanic stability of the *S. acidocaldarius* S-layer, it was possible to produce empty cells (ghosts) consisting only of the outermost S-layer membrane and to study their interactions with U(VI) at highly acidic (pH 1.5 and 3.0) and at moderate acidic (pH 4.5 and 6.0) conditions. Applying a set of modern spectroscopic techniques such as Time-Resolved Laser-induced Fluorescence (TRLF), X-ray Absorption, and Fourier-Transformed Infrared (FT-IR) we were able to demonstrate that at highly acidic conditions the *S. acidocaldarius* S-layer does not play any protective role against the toxic U(VI). At these conditions low amounts of uranium are bound mainly by the phosphate groups of the cytoplasmic membrane [5]. This finding is in distinction to the results obtained with S-layers of the bacterial isolates recovered from uranium mining wastes. The S-layers of the latter bind significant amounts of U(VI) and strongly contribute to the remarkable uranium resistance of their hosts [6]. The high capability of the mentioned bacterial S-layers to bind U(VI) was attributed to the fact that they are phosphorylated [6]. This feature is unusual for both bacterial and archaeal S-layers and is not the case for the S-layer of *S. acidocaldarius* [6, 7]. At moderate acidic conditions (pH 4.5), typical for most uranium mining wastes, the studied archaeal S-layer ghosts, again in contrast to the bacterial ones, bind insufficient amounts of U(VI) exclusively via the carboxylic groups of their carboxylated amino acid residues [7]. At pH 6.0, which is substantially above the growth optimum of *S. acidocaldarius*, the permeability of its cells is increased due to the pH stress and possibly also to the presence of U(VI). As a result uncontrolled uptake of U(VI) as well as release of phosphorylated biomolecules and also of orthophosphate occurs. These processes result initially in formation and precipitation of mixed uranyl phosphate phases. With time most part of U(VI) is biomineralized in inorganic mineral phases. The efficacy of the biomineralization processes is, however, much lower than those published for bacteria, possibly due to the lower amount of polyphosphatic bodies in the studied archaeon [8]. We suggest that the limited presence of archaea in uranium wastes is related to their lower resistance to U(VI) which is determined by their cell wall structure and possibly also by some particular physiological and biochemical characteristics.

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Novel Thermochronometric Techniques Applied to the Lavrion Detachment, Lavrion Peninsula, Attica, Greece

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The Lavrion Peninsula (SE Attica) is situated at the western boundary of the Attic-Cycladic Crystalline Complex (ACCC). The ACCC underwent blueschist to eclogite facies metamorphism during the Eocene followed by a greenschist facies overprint coincident with broad regional extension during the Miocene. This extension is generally attributed to the process of slab rollback and led to the formation of crustal scale detachments in the Aegean. In Lavrion, the dominant structure is a sub-horizontal detachment which juxtaposes lower plate rocks of the Kamariza Unit against the Lavrion Unit of the upper plate. Both units are dominated by greenschist facies calc-schists and marbles. The Lavrion Detachment (LD) is defined by a mylonitic zone which displays a top-to-SSW sense of shear. This is consistent with the overall sense of shear of the larger West Cycladic Detachment System (WCDS) exposed on the islands of Kea, Kythnos, Serifos and Makronisos directly to the east of the Lavrion Peninsula. The LD, therefore, may represent the western most exposure of the larger WCDS. Exhumation of lower plate rocks along the WCDS on Kea, Kythnos, and Serifos occurred between 5-8Ma, 11-15Ma, and 5-8Ma, respectively^[1]. In order to further constrain timing of movement on the LD and how it correlates to the WCDS, (U-Th)/He dating was conducted to understand the low temperature evolution of the lower plate and proximal upper plate rocks. Many upper and lower plate rocks (e.g. low grade calc-schists and marbles) of the LD are not conducive to traditional low temperature thermochronometric techniques so this study will employ titanite (U-Th)/He dating coupled with zircon and apatite (U-Th)/He where appropriate lithologies are present. Titanite is a common phase in greenschist facies calc-schists and possesses a closure temperature similar to zircon, making it an ideal chronometer for this study.^[2]

[1] Grasemann (2012) *Lithosphere* **Volume 4**, 23-39.

[2] Reiners (1999) *Geochimica et Cosmochimica Acta* **Volume 63**, 3845-3859.