ESRF	**Experiment title:** **Investigation of Thorium(IV) and Uranium(IV) Silicates: colloid formation - alteration - solid state characteristics**	**Experiment number**: 20-01-723
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Report:

The project intends to reveal specific properties of U(IV) and Th(IV) silicate colloids in aqueous solution as well as related microcrystalline solid solutions. The role of silica as stabilizing factor for Th(IV) and U(IV)/silica colloids is known, but structural implications are under investigation. We report here on results to identify α-$ThSiO_4$ and β-$ThSiO_4$.

Metal-Metal interactions in highly disordered Th/silica colloids show in EXAFS spectra usually only weak signals due to destructive interference of the individual backscattering waves [1]. Such a destructive interference has been described by Rothe et al. for actinide oxyhydroxides [2]. The effect of disorder on the height of the Th-Th peak was investigated using the EXAFS spectra of α-$ThSiO_4$ and β-$ThSiO_4$ (Fig. 1). α-$ThSiO_4$ crystallizes in the tetragonal space group 4_1/amd, and shows, according to this high symmetry, four identical Th-Th distances at 3.90 Å. ß-$ThSiO_4$ occurs in the monoclinic space group P 2_1/n and has, due to this low symmetry, six different Th-Th distances (2 x 4.08 Å, 1 x 4.12 Å, 2 x 4.26 Å, and 1 x 4.30 Å). It is evident that high-symmetric α-$ThSiO_4$ exhibits EXAFS features including a well resolved Th scattering peak whereas the EXAFS spectrum of low-symmetric ß-$ThSiO_4$ shows only the first scattering signals and a rather disturbed signal from Th-Th interactions. This problem can be overcome by using X-ray scattering where the differential contributions of the individual scattering pairs are summarized to a total scattering signal. Real-space analysis of X-ray scattering data is sensitive to local

structure even in case of structural disorder [3]. The lower part of Fig. 1 shows the High-energy X-ray scattering (HEXS) pair distribution functions g(R) obtained for α-$ThSiO_4$ and β-$ThSiO_4$. For both structures, the pair-distribution functions of HEXS show a strong Th-Th scattering signal. The experimental resolution is not high enough to differentiate between individual Th-Th distances in β-$ThSiO_4$, but the distal distribution causes a clear peak broadening related with the different Th-Th distances in the structure.

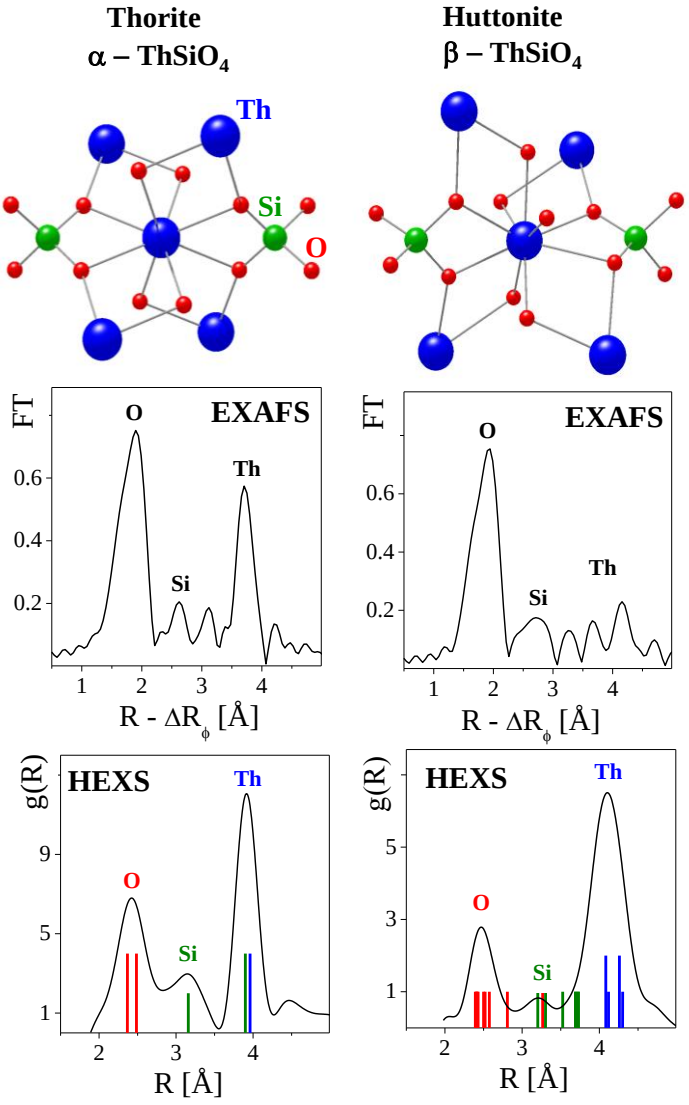

Fig. 1. Comparison of Th L_3 EXAFS and the pair distribution function g(r) obtained from high-energy X-ray scattering (HEXS) of α-$ThSiO_4$ (left), and β-$ThSiO_4$ (right). At the top a simplified structure of the next neighbor coordination environment is presented, followed below by the Fourier transform of the Th L_3 EXAFS spectra, and at the bottom the pair distribution function obtained from HEXS. The colored lines are a histogram of the next neighbor distribution obtained from crystal structure data

References

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[3] Egami T. and Billinge S.J.L. (2003) *Underneath the Bragg peaks – structural analysis of complex materials.* Pergamon.