Redox and Speciation of Uranium in Al-Rich Perovskites from High-Pressure/High-Temperature Conditions

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Abstract. Macro-, and microXANES and EXAFS spectra were collected at the U-L_3, Al-K, Si-K and Ca-K edges in high pressure/high temperature $CaSiO_3$ perovskite that aim to simulate one potential reservoir for the Earth heat flow. In that perovskite, U is tetravalent and appears substituted to Ca thanks to a coupled substitution of Al for Si. A FEFF model of the Ca site occupied by U is consistent with that mechanism but the modeled EXAFS spectrum is markedly different to that measured in various samples at various scales (mm and µm). Structural relaxation of the U site probably explains these discrepancies, suggesting that, if ionic rules can explain qualitatively cation substitutions, more complex mechanisms occur at the Å-scale.

Keywords: uranium, thorium, perovskite, ceramics, deep Earth, XANES, EXAFS
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INTRODUCTION

The origin of the Earth's source of heat is a major area of research in geophysics because it drives the Earth's first order activity such as plate tectonics (among others). The decay of nucleides (K, Th and U) is among the most solicited model to explain this heat flow [1]. Recent partitioning experiments showed that some scarce Al-bearing silicate Ca-perovskite-type compounds can host some quantities of actinides [2]. Such a phase in the lower mantle could behave as a "sink" for radionucleides in the deep Earth. This radiogenic bearing phase is a good candidate to be part of a recently proposed dense layer from 1600 to 2900 km depth at the basis of the lower mantle [3-4]. This layer would incorporate all the radiogenic elements of the lower mantle and provide a bottom heating of our planet. In this study, we present a XAFS, µ-XAFS and µ-XRF study of a new U-bearing perovskite synthesized at high pressure and temperature (Fig. 1).

EXPERIMENTAL

U-bearing Ca-perovkites ($Ca(Si,Al)O_3$) samples were synthesized at 18 GPa and 2000 K (for 12 hours) then quenched in a 1000 ton multi-anvil apparatus (French national facility, Clermont-Ferrand), with conditions detailed elsewhere [5]. These samples show variations in perovskite chemistry as well as in actinides (Th and U). Sample MA-323 has 3. mol.% U. U-L_3 edge XANES and EXAFS spectra were collected using Si(220) double-crystal monochromators on beamline 11-2 (SSRL, Stanford, USA) to k=15 $Å^{-1}$. A "Lytle" detector was used to collect the spectra in the fluorescence mode. U-L_3 µ-XANES spectra were

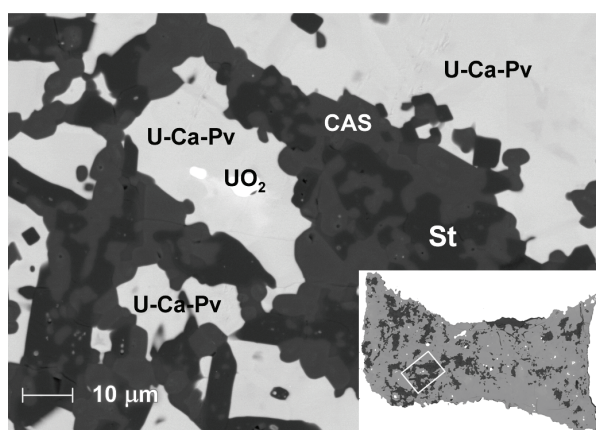

FIGURE 1. Detail of the backscattered image of sample MA-323 shown in the inset. U-Ca-Pv, CAS, St and UO_2 refer to the U-bearing $CaSiO_3$ perovskite, $CaAl_4Si_2O_{11}$ ceramic, stishovite and some remaining UO_2 inclusions, respectively.

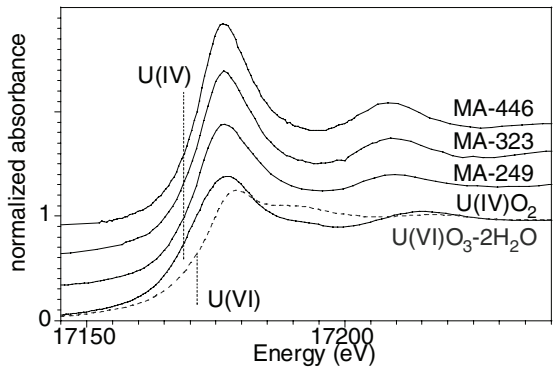

FIGURE 2. U-L_3 macroXANES for three U-bearing $CaSiO_3$ samples, As compared to UO_2 (U^{4+}) and metaschoepite (U^{6+}).

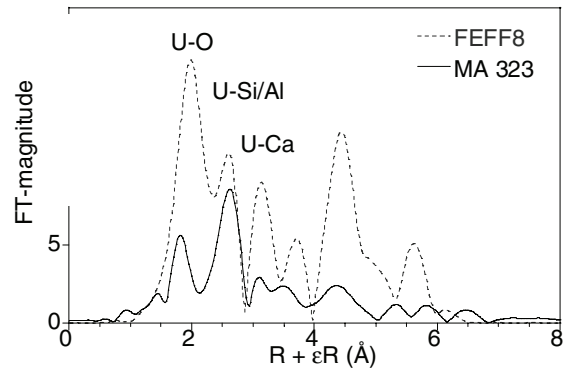

FIGURE 4. Fourier transforms for the sample MA 323, as compared to that obtained for a FEFF simulation of U in the Ca-site of $CaSiO_3$.

collected on the ID22 beamline using a Si(111) monochromator (15x10 µm beam). Finally, Al-K, Si-K and Ca-K µ-XANES and µ-XRF spectra (10x7 µm beam) were collected in the fluorescence mode at the LUCIA beamline (SOLEIL-SLS). All experiments were carefully checked in energy, thanks to the use of models (UO_2, metaschoepite, alumina, quartz and calcite). XANES and EXAFS spectra were reduced using conventional methods as outlined in the "xafs" package [6].

RESULTS AND DISCUSSION

Macro-EXAFS collected at the U-L_3 edge show that U is tetravalent in the three perovskites investigated at SSRL (Fig. 2). In these minerals, the U-L_3 edge crest is particularly intense as compared to that for UO_2. This suggests that U occupies a site with coordination greater than that of UO_2. The analysis of the k^3-weighted EXAFS and its Fourier Transform (FT) confirms that most of the initial UO_2 was dissolved and incorporated into the perovskite structure (Fig. 3). FEFF models [7] for the 2 possible sites for this actinide in that perovskite were computed using a crystal structure refinement (Rietveld) of the hosting perovskite with U for the central atom (Fig. 4). The best agreement is obtained when U is located in the dodecahedral site (12-coordinated). This is in agreement with the intensity of the U-L_3 XANES "white line" feature for these perovskites. Because the agreement between the FEFF simulation of the Rietveld refinement and the experiment is far from perfect, further structural models are underway. To check the chemical and speciation homogeneity of these particularly small samples (150x100 µm), µ-XRF (excitation at 18 KeV) and µ-XANES (at the L_3-edge) were collected at the ID22 beamline, at the ESRF. Figure 5 shows a map of the U-Lα fluorescence for a selected area of one perovskite sample (U-$CaSiO_3$ perovskite; Fig. 6). The map shows that the U concentration is variable throughout the sample. Some residual U-rich aggregates are observed, most likely residual UO_2. However, these domains are rare. Most of U is located within the perovskite, consistent with macro-XANES spectra collected at SSRL. Despite of its heterogeneities, U is dominantly tetravalent in all perovskites. To obtain robust stoechiometric constraints between U, Ca, Si and Al, µ-XRF

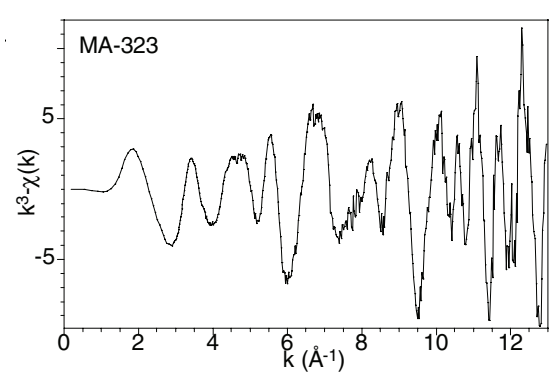

FIGURE 3. U-L_3 macroEXAFS spectra collected for sample MA 323.

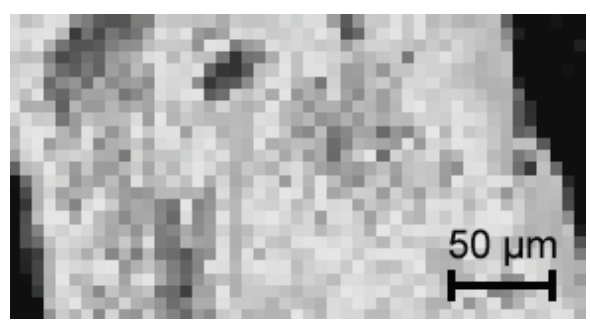

FIGURE 5. U-Lα mapping (grey) of the #323 U-perovskite, showing unsuspected heterogeneities (∅ 20 µm) (grey to white). In black is the Pt casing material used for the HP-HT synthesis. Each pixel is 4x6 (HxL) µm in size.

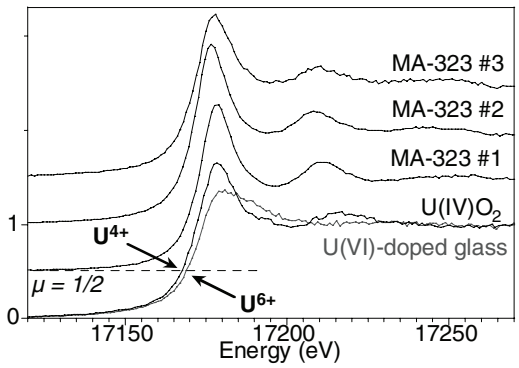

FIGURE 6. μ-XANES of L_3-U collected for U-bearing Ca-perovskite, with uraninite UO_2 as a standard for U^{4+} and U-doped wollastonite as a standard for U^{6+}.

(excitation at 5 keV) and μ-XANES spectra were collected at the LUCIA beamline (SOLEIL, SLS). We find elemental correlations between U-Lα and Ca-Kα (the largest cations) on one side and between the K_a of Si and Al, (the smaller cations) on the other side (Fig. 7). Elemental correlations (μ-XRF) between (Ca+Th+U) and (Si+Al) for a 60x60 map of the perovskite #323 (excitation: 5 keV; LUCIA beamline). We observe clearly three populations/mechanisms; (1) is a phase rich only in Si/Al (most likely stishovite — or SiO_2—; see Fig. 1); (2) is a phase with a constant Si/Al ratio, with an highly variable content in Ca/U, either high or low (low and high-U perovskite); (3) is a phase in which (Al,Si) and (Ca,U) are anti-correlated (most likely the $CaAl_4Si_2O_{11}$ ceramic; see Fig. 1). The origin of this third population is still not elucidated. This correlation is a direct evidence for a coupled substitution model involving (Ca,U) and (Si,Al). This is confirmed by the similarities of the Al- and Si-K-edge XANES spectra for selected spots of that perovskite (Fig. 8). As compared to a variety of model compounds, the "white line" of the Al-, and Si K-edges in the U-perovskite suggests that these cations

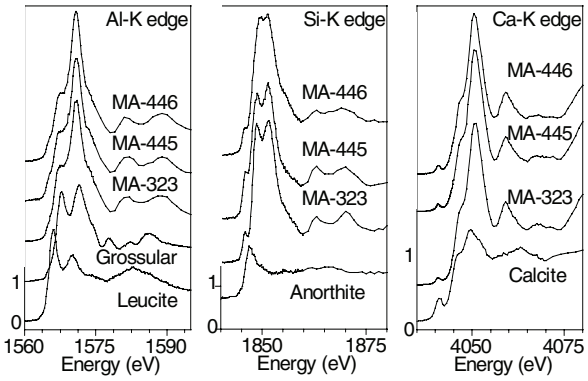

FIGURE 8. Ca-K, Al-K and Si-K μ-XANES spectra collected for the U-bearing Al-$CaSiO_3$ perovskite. The Ca K-edges XANES for the perovskite are significantly different from those from Si-K and Al-K.

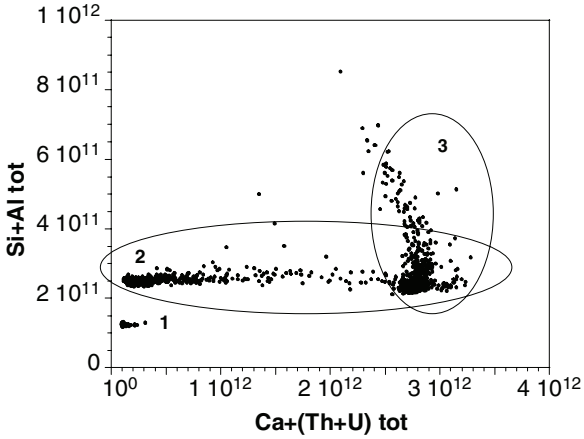

FIGURE 7. Elemental correlations (μ-XRF) between (Ca+Th+U) and (Si+Al) for a 60x60 map of the perovskite #323 (excitation: 5 keV; LUCIA beamline).

are 6-coordinated. In contrast, the Ca K-edge XANES cannot be compared directly to the U-L_3 edges of U because of differences of selection rules (K vs. L_3).

CONCLUSIONS

MacroXANES/EXAFS and μ-XANES spectra for U-bearing perovskite show that U remains tetravalent in the $CaSiO_3$ perovskite that occur in the lowermost part of the Earth's transition zone. μ-XRF correlations suggest that the substitution process is valid for a wide range of actinide concentrations, up to ~20 times more diluted. This suggests that our results can be extrapolated to the deep Earth, in which the average actinide concentrations are in the ppm range. The exact location of actinides in these Al-perovskites reflects simple ionic radii considerations. However, *ab-initio* models of the XAFS spectra (FEFF 8.2) calculations shows that U does not substitute ideally to Ca without a significant structural relaxation, that cannot be detected by a Rietveld refinement (μ-X-ray diffraction) of these exact samples. Preliminary U-site relaxation using *ab-initio* methods are underway to understand the exact substitution mechanism.

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