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Coordination of Actinides in Silicate Melts

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Abstract: The structural environments around Th(IV) and U(VI) at concentrations ranging from 90 ppm to 7 wt.% were investigated in glasses and melts of Na di- and trisilicate compositions between 293 and 1550 K using x-ray absorption fine structure (XAFS) spectroscopy. Data for model compounds were collected at temperatures up to 2000 K in order to quantify the magnitude of anharmonic effects. Data for glasses and melts were collected and analyzed considering anharmonic (cumulant-expansion), curved-wave and multiple-scattering effects. In the glasses and melts studied, U(VI) occurs as uranyl groups [d(U(VI)-O = 1.78 and 2.25(3) Å] and Th(IV) occurs as a mixture of 6- and 8-coordinated Th at the 1-3 wt.% Th level, but as 8-coordinated Th at trace levels (90-1000 ppm). These two actinides do not undergo significant coordination changes during the glass-to-melt transformation. However, special care in the data analysis protocol is needed to avoid the effects of anharmonicity (due to both positional and thermal effects) which tend to artificially increase the (apparent) amount of 6-coordinated Th.

1. INTRODUCTION

Naturally occurring actinides (Th and U) are important trace elements that are used to model the evolution of magmas (molten volcanic rocks) within the deep Earth's crust [1]. These elements are also important in glass-based nuclear wastes. Actinide-bearing silicate glasses have long been considered as structural analogs of their molten modifications. In this study, we report the first Th- and U-L_{III} XAFS data collected in-situ, at high temperatures in molten silicates. Th is used to model the behavior of tetravalent actinides (Th and also U(IV)), whereas U is relevant to more oxidized actinide ions that form special complexes (U(VI) as uranyl, Np(V) as neptunyl, etc.).

2. EXPERIMENTAL

Two simple glass compositions were studied: Na-di-, and trisilicate (NS2: Na₂Si₂O₅ and NS3: Na₂Si₃O₇). In parallel, a set of Th(IV) and U(VI) model compounds were examined (e.g., ThO₂, α-ThSiO₂, UO₂, cuproskłodowskite, β-uranophane, and others). Th- and U-L_{III} XAFS spectra for model compounds were collected in transmission mode at LURE (Orsay, France) using the energy dispersive (XAS10) spectrometer and a Si-(311) bent monochromator crystal. We used the heating wire technique to collect XAFS spectra every 20 K steps, up to 2000 K [2]. Temperature was measured using an optical pyrometer as well as using a power-temperature calibration based on a set of model compounds melting points. The DCI storage ring was operating at 1.8 GeV and 100-300 mA positron current. XAFS data for the glasses and melts were collected on beam line 4-3 at SSRL (Stanford) with a Si-(220) two-crystal monochromator; the SPEAR storage ring was operating at 3 GeV and with 50-100 injected electron current. We used a high temperature Pt₉₀Rh₁₀ heater to collect XAFS data in the fluorescence mode up to 1550 K [3]. Temperature was measured in-situ the glass/melt sample by using a Pt/Pt₉₀Rh₁₀ thermocouple.

XAFS spectra were corrected for background absorption using a Victoreen function and normalized for absorbance using a spline fitting. The normalized EXAFS oscillations were converted into k-space by choosing E₀ "half-way" up the

Fig. 1 Normalized Th-L_{III} EXAFS for selected glasses and melts (see Fig. 2 for legend).

Fig. 2 Fourier Transforms of the Th-L_{III} EXAFS for selected glasses and melts.

Fig. 3 Th-L_{III} XANES for NS2 glass and melt with 90 ppm Th.

Fig. 4 U-L_{III} XANES for NS2 glass (*T°* in italic char.) melt (*T°* in non-italic) with 3 wt.% U(VI).

absorption jump. The EXAFS oscillations were Fourier Transformed (FT) over the range 3-12 Å⁻¹ using the Kaiser filter and k³-weighted. The contribution arising from Me-O pairs (Me=Th or U) was Fourier filtered in the range 1-2 Å prior to fitting, which utilized a curved-wave, anharmonic (cumulant expansions) formalism [3] that has proven successful in modeling thermal expansion and anharmonicity for Th-O and U-O bonds in the model compounds previously reported, up to 2000 K. Empirical amplitude and backscattering phase-shifts were extracted from ThO₂ and uranyl acetate-trihydrate.

3. RESULTS

3.1. Th(IV)

EXAFS data for model compounds α-ThSiO₄ and ThO₂ (in which Th(IV) is 8-coordinated) were collected up to 2000 K. There is little evidence for temperature induced-anharmonicity in these compounds, a result that is consistent with the relatively high Th-O bond valence (0.5 valence units) which results in relatively low thermal expansion coefficients. However, anharmonic EXAFS analysis for Th in melts at appears necessary even though anharmonicity is rather limited.

Figs. 1-3 show typical Th-L_{III} EXAFS, FT and XANES spectra collected for NS2 glasses and melts with Th-contents between 3 wt.% and 90 ppm. At room temperature, Th(IV) shows average anharmonic Th-O distances of 2.35(3) Å in NS2 and NS3 glasses with 3-7 wt.% of Th. This suggests the presence of a mixture of 6- and 8-coordinated Th(IV). Compared to previous work, the present EXAFS results give slightly higher average Th-O distances, suggesting that 6-coordinated Th(IV) may be less important than previously taught. Instead, 8-coordinated Th(IV) appears to be the dominant species. In melts (above 800 K), the XANES or EXAFS spectra don't show any changes: Th remains mostly 6- and 8-coordinated in these melts. For glass and melts with lower Th-concentrations (0.1-1 %), we found that 8-coordinated Th(IV) predominates over 6-coordinated Th(IV). We also collected Th-XANES spectra in a melt containing 90 ppm Th at 1520 K. The XANES are similar to that of a glass with 1000 ppm Th, again suggesting that 8-coordinated Th predominates in this melt.

3.2. U(VI)

Unfortunately, we found that the U-L_{III} EXAFS data were extremely noisy at temperatures above 600 K; therefore only XANES spectra were collected, even for model compounds. However, the U-L_{III} XANES of U(VI) in glasses is rich in information because of the presence of uranyl groups (UO₂O₄₋₆). FEFF6 calculations [4] show that feature B in the XANES of uranyl complexes (Fig. 4) is due to axial oxygens. At all temperatures, we found this feature to be present at the same position, suggesting little change in the U-O_{axial} distance for glasses and melts (≈ 1.78 Å). This result suggests that uranyl groups are also present in the molten state, in an environment similar to that of the glass. Also, changes in the U-concentration (0.2-7 wt. range) don't have a significant effect on the U-L_{III} XANES, confirming again the high stability of these uranyl complexes in the melts studied here.

4. DISCUSSION

Compared to their glassy modifications, we observed little changes in the coordination environment of Th(IV) and U(VI) in NS2 and NS3 melts in the 700-1550 K range for actinide concentrations ranging from 0.01 to 7 wt.%. Th(IV) is mostly 6- and 8-coordinated but, surprisingly the 8-coordinated Th species dominates at lower Th-contents. This coordination chemistry is very similar to that observed for synthetic glasses simulating natural magmas where a mixture for 6- and 8-coordinated Th was detected [1]. This suggests that natural magmas (in which the Th-concentration is around the ppm level) may contain mainly 8-coordinated Th(IV). Six-coordinated Th(IV) has been reported for nuclear waste glasses (which have a composition not far from NS2 and NS3) [5]. The present study indicates that 6-coordinated Th(IV) may also be important in these systems. Also increasing temperature does not promote any nucleation around Th or U in NS2 and NS3.

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References

- [1] Farges F., *Geochim. Cosmochim. Acta* **55** (1991) 3303-3319; Farges F., Ponader C., Calas G. and Brown G.E. Jr, *Geochim. Cosmochim. Acta* **56** (1992) 4205-4220 (see also references therein).
- [2] Farges F., Figuet G., Itie J.-P. and Andrault D., *Nucl. Instr. Meth. Phys.* **101** (1995), 493-498.
- [3] Farges F., Brown G.E. Jr., Navrotsky A., Gan H. and Rehr J.J., *Geochim. Cosmochim. Acta* **60** (1996), 3023-3065 (3 papers).
- [4] Zabinsky S.I., Rehr J.J., Ankudinov A., Albers R.C. and Eller M.J., *Phys. Rev. B* **52** (1995), 2995-3009.
- [5] Veal B.W., Mundy J.N. and Lam D.J., Actinides in silicate glasses, "Handbook on the Physics and Chemistry of the Actinides", (A.J. Freeman and G.H. Lander, Eds.), pp. 271-309. Elsevier.