URANIUM REDOX EQUILIBRIA IN INTERACTION WITH CHROMIUM IN MOLTEN SILICATES. Henry D. Schreiber and G. Bryan Balazs, Department of Chemistry, Virginia Military Institute, Lexington, VA 24450.

The redox equilibria of uranium in synthetic silicate melts have been previously investigated as a function of the synthesis conditions in attempts to understand the geochemical behavior of uranium [1,2]. However, these studies were somewhat idealized in that uranium was the only multivalent metal present in the melts. Melts that mimic simplified basaltic magmas should contain a potpourri of redox components, in particular metals such as iron, chromium, europium, etc. Thus, it becomes imperative to determine the effects of other multivalent elements on the redox equilibria of uranium and to interpret such effects with respect to the geochemical properties of uranium. As an initial step, the interactions of chromium via its Cr(VI)-Cr(III)-Cr(II) equilibria with the U(VI)-U(V)-U(IV) equilibria in synthetic silicate melts are investigated.

The redox equilibria of uranium and of chromium have individually been defined in silicate melts of composition FAS (53 wt% forsterite, 27 wt% anorthite, & 20 wt% silica) and FAD (25 wt% forsterite, 6 wt% anorthite, & 69 wt% diopside). These previous results [1,3] are summarized in figure 1 as a series of redox couples in order of reduction ease in silicate melts: Cr(VI)-Cr(III) > U(VI)-U(V) > U(V)-U(IV) > Cr(III)-Cr(II).

Homogeneous glass powders of base compositions FAS and FAD doped with uranium and chromium oxides were prepared by multiple fusions, quenchings, and grindings. The individual samples were synthesized at 1500°C over a range of oxygen fugacities using a controlled atmosphere furnace. The melts were then rapidly quenched to glasses to preserve the redox states for analyses. Optical absorption spectra of the sectioned, polished glass slabs from the samples were recorded from 300 nm to 3000 nm.

The absorption spectra of glasses individually doped with either chromium or uranium are shown in figure 2. Whereas all three chromium redox states absorb rather strongly in the near-UV/visible region for the glasses, uranium absorbs much weaker from the near-UV to the near-IR. Of particular concern are the near-IR absorption bands of U(IV) and U(V) whose peak intensities have been calibrated to the absolute concentrations determined by redox analyses [1], as per a Beer's law plot shown in figure 3. These near-IR peaks of U(IV) and U(V) should be capable of monitoring the respective ions' concentrations without interference from chromium absorptions in the dual-doped glasses. Representative spectra of the glasses simultaneously possessing uranium and chromium are shown in figure 4. Although the visible portion of the spectra would be difficult to resolve into the individual chromium absorptions, the near-IR portion is very straightforward to interpret.

Via this spectrophotometric technique, the U(IV) and U(V) concentrations can be directly obtained, while the U(VI) concentration can be obtained by difference, for the dual-doped glasses. These preliminary measurements are expected to be complemented by EPR methods [4] to monitor directly the chromium redox states as well. A semi-quantitative treatment of the visible spectra in terms of the [Cr(II)]/[Cr(III)] ratios in the glasses are nevertheless consistent with the uranium results. The results of the uranium redox analyses, which provide insight into the chromium-uranium mutual interaction, are displayed in figure 5. Cr(VI) in the silicate melt appears to oxidize both U(IV) and U(V) to the U(VI) state; Cr(III) also appears to reduce U(V) and U(VI) to U(IV) in the melt. The interactions of these chromium species with the uranium redox states seem to proceed essentially to comple-
URANIUM REDOX EQUILIBRIA

Schreiber, H. D. and Balazs, G. B.

Since terrestrial magmas possess chromium as Cr(III) while lunar and some meteoritic basalts possess chromium as both Cr(II) and Cr(III) [3], it might be expected that uranium would exist as U(VI) and U(V) [B] in the former systems and as U(IV) [C] in the latter systems. However, further interaction of the uranium redox states with the Fe(III)-Fe(II) redox couple in terrestrial situations might be predicted to shift the uranium equilibria in the direction of U(IV) in these magmas.


FIGURE 1: Redox equilibria of various elements in composition FAD. \( R \) is the ratio of reduced to oxidized ion concentrations.

FIGURE 2: Optical absorption spectra of glasses containing chromium or uranium. Positions of absorption bands in nm: Cr(VI) - 360, Cr(III) - 440, 640. Cr(II) - 435, 630. U(VI) - 425, 500. U(V) - 825, 1350, 1410, 1650. U(IV) - 450, 500, 640, 900, 1030, 1880.
URANIUM REDOX EQUILIBRIA

Schreiber, H. D. and Balazs, G. B.

FIGURE 3: Calibration of near-IR peak intensities with uranium redox concentrations. Base compositions ADA-1 and ADA-2 are described in [2]. $E = \text{Absorbance} \div \text{sample path length (mm)}$.

FIGURE 4: Optical absorption spectra of glasses simultaneously containing Cr and U.

FIGURE 5: Stability region of Cr and U redox state with respect to the imposed oxygen fugacity.