THE REDOX STATES OF URANIUM IN SYNTHETIC BASALTIC MAGMAS. Henry D. Schreiber and Stephen M. Andrews, Department of Chemistry, Virginia Military Institute, Lexington VA 24450

An understanding of the oxidation-reduction chemistry of uranium in magmas is necessary in order to interpret correctly the observed distribution of uranium in planetary basalts [1]. Evidence that U(VI), U(V), and U(IV) are all viable redox species of uranium in molten silicates [2] provides a foundation for this understanding. The objectives of this study is to quantify the redox relationships of uranium in silicate analogs of magmas, and thus to determine the role of the redox state of uranium on the observed geochemistry of uranium in basalts.

Homogeneous glass powders of two base compositions FAS = 53.0 wt% forsterite, 27.1 wt% anorthite, and 19.9 wt% silica; FAD = 24.4 wt% forsterite, 6.2 wt% anorthite, and 69.4 wt% diopside [3] doped with about 0.8 wt% total uranium were prepared by multiple fusions, quenchings, and grindings. Individual samples were then synthesized by equilibration of about 250 mg of glass powder for 24 hours at a certain temperature (1500°C; 1550°C1) and oxygen fugacity (-log fO2 = 0 to 10) followed by a rapid quench of the melt to a glass [3]. That redox equilibrium had been established was ascertained by time studies. All glass samples were then analyzed by indirect chemical redox titrations [3] to determine the amount of "reduced" uranium redox species. Total uranium contents and major element contents of the individual glasses were checked by electron microprobe analyses.

The experimental results are summarized in figure 1. Since the data did not correspond to a simple U(VI)-U(IV) redox equilibrium, equilibria involving U(VI)-U(V)-U(IV) were assumed to be present in the melts. An excellent fit of the experimental data with this multiple equilibria model was attained. No evidence for the existence of U(III) in the samples was obtained. The effect of base composition FAS being more reducing than composition FAD for the uranium redox equilibria agrees with compositional effects on other redox couples [3]. Figure 2 compares the uranium equilibria with the equilibria of other one-electron redox couples in molten silicates. Although the degree of reduction of each redox couple in a silicate melt depends on the particular synthesis conditions, the relative order of the redox equilibria remains constant when referred to a common base composition, temperature, and oxygen fugacity. In order of ease of reduction in the molten silicates: Ce(IV)>Ce(III) > U(VI)>U(V) > Fe(III)>Fe(II) > U(V)>U(IV) > Cr(III)>Cr(II) > Eu(III)+Eu(II) >> Ti(IV)+Ti(III).

Clearly U(IV) is the predominant uranium redox species under reducing conditions, for example lunar environments, in basaltic magmas. However, U(V) might be an important redox state in magmas under more oxidizing conditions. Interactions of the uranium redox equilibria with the controlling Fe(III)-Fe(II) equilibrium in natural magmas may in fact further stabilize the U(V) state, upon analogies to the interactions of iron with other synthetic redox systems in molten silicates [5]. In addition, the experimental results are extended to predictions concerning the redox chemistry of plutonium in figure 3. Whereas the trivalent redox state of uranium is not predicted, nor found, to the stable in silicate melts even under reducing conditions, the trivalent redox state of plutonium is expected to predominate under conditions that approximate those of lunar basalts. The Pu(III) species was previously postulated to exist on the basis of the distribution of plutonium in synthetic systems [1].

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Schreiber, H.D., et.al.


FIGURE 1: Summary of the experimental data for the U(VI)-U(V) and U(V)-U(IV) redox equilibria in synthetic silicate melts as a function of base composition, oxygen fugacity, and temperature. Constraints placed on the data in order to produce the graphs were the total uranium contents, the redox titration analyses, and the simultaneous fits of the -log f_\text{O}_2 versus log R \{where R = [U(V)]/[U(VI)] and [U(IV)]/[U(V)]\} relationships to straight lines of slope 4. X: reduced ion = [U(V)]/([U(VI)] + [U(V)]) and [U(IV)]/[U(V)] + [U(IV)].
FIGURE 2: The redox equilibria of U(VI)-U(V) and U(V)-U(IV) in silicate melts compared to those of Ti(IV)-Ti(III), Eu(III)-Eu(II), Cr(II)-Cr(II), Fe(III)-Fe(II), and Ce(IV)-Ce(III) [3,5]. The grossular summary [2], although meant to be only semiquantitative, shows good agreement with this study. $R = \text{ratio of reduced to oxidized ion concentrations}$, while $X_{\text{reduced ion}} = \text{fraction of the element in its reduced state}$.

FIGURE 3: Relationship of M(IV)-M(III) and M(V)-M(IV) equilibria in molten silicates to standard aqueous reduction potentials ($E^o$). All silicate data have been normalized to conditions that approximate those of an average lunar magma as defined previously [3]. $\log R$ and $X_{\text{reduced ion}}$ are as defined in figure 2. $E^o$ values are from [6]. Points represented by solid circles are from studies by this author, while open triangles are from [7].