An electrochemical series of redox couples has been developed in a silicate melt that models basaltic magmas [1]; this scale of redox couples ordered in terms of reference reduction potentials allows the prediction of the fraction of each redox ion as a function of the imposed oxygen fugacity at a given temperature and composition. It was determined that the order of the redox couples in this electrochemical series is relatively insensitive to the melt composition, so that accordingly the series is applicable to many basaltic systems.

The melt composition controls the oxide ion activity or basicity of the melt. As the melt basicity increases, the redox equilibria should shift to increase the fraction of the oxidized redox ion at the expense of the reduced ion [2]. In order for an electrochemical series of redox couples to retain the same ordering of the couples independent of the composition, the redox equilibria of each element must then shift by the same percentage with a change in the composition or oxide ion activity.

OBJECTIVE. The purpose of this study was to test the hypothesis that the position of a redox couple in an electrochemical series does not change significantly as a function of silicate melt composition. Although the absolute value of the reference reduction potential \( E' \) is expected to vary with composition, the ordering of the \( E' \) scale should remain generally invariant. In this regard, four redox couples \{Ce(IV)-Ce(III), U(VI)-U(V), Fe(III)-Fe(II), V(V)-V(IV)\} have been employed to monitor the redox chemistry in a series of diopside-albite melts.

EXPERIMENTAL PROCEDURES. Five base compositions (figure 1) that spanned pure diopside to pure albite were prepared by the fusion of component oxides and carbonates. As the melt increases in the proportion of albite end member, the fraction of the acidic components increases. Consequently, the melt becomes more polymerized as indicated by the viscosity increase [3] and the non-bonding oxygens (NBO) decrease [4]. Thus, the diopside melts should be more oxidized than the albite melts.

Homogeneous glasses of the five base compositions containing each multivalent element were prepared by fusion of the diopside-albite glass powder and multivalent element oxide. Individual samples were then equilibrated under reference conditions (\( T = 1425^\circ \text{C}, f_{O_2} = \text{air} \)) for 24 hours and subsequently quenched to glasses. Near-infrared/visible spectra of glass slabs were obtained to monitor concentrations and coordination sites of specific redox ions. Redox microtitrations on the samples were employed to determine reduced to oxidized ion concentration ratios in the glasses [5].

RESULTS. The redox ratios of the four multivalent elements as a function of the melt composition (at constant temperature and oxygen fugacity) are shown in figure 2. As the diopside component of the melt is replaced by the albite end member; the redox states of uranium and cerium do not change appreciably, whereas both iron and vanadium becomes more reduced. A vanadium-rich phase, probably a vanadium oxide, separates from the vanadium-containing albite melt. Figure 2 also illustrates that the reference reduction potentials \( E' \) of the four redox couples remain in the same order for all compositions in the diopside-albite series.

The concentration of a particular redox ion and its coordination site within the glass structure can be ascertained by its absorbance intensity.
and position, respectively, in the electronic spectrum (Figure 3). The absorption peaks for Fe(II) and V(IV) systematically increase in intensity with an increase in albitic concentration in the melt, indicative once again that the reduced ions are preferentially stabilized in the albite melts. Changes in the wavelength of the absorption maxima for these two ions with composition represent changes in their coordination sites [6]. The near-infrared spectrum of uranium-doped glasses shows a systematic change of percentages of U(V) in an octahedral site with tetragonal distortion (predominant in diopsidic melts) to U(V) in UO₂ complexes (predominant in albitic melts) [7]. However, even with a dramatic change in coordination of the U(V) ion in the composition series, the [U(V)]/[U(VI)] does not appreciably change in these melts.

CONCLUSIONS. Although melt composition directly affects the redox equilibrium of a multivalent element, it has a tendency to affect each redox couple similarly. Thus, the scale of relative reduction potentials E̅M developed for use in silicate melts appears to be quite applicable to most complex melts. The electrochemical series of E̅M indeed provides a measure of the inherent ease of reduction of redox couples in melts which can model a range of basaltic compositions.