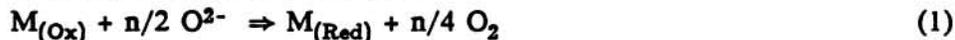


**REDOX RELATIONSHIPS IN SILICATE MELTS AND SILICATE MELT STRUCTURE** R. O. Colson and C. R. Keedy, Dept. of Earth and Planetary Sciences & McDonnell Center for the Space Sciences, Washington University, St. Louis, MO 63130.

Knowledge of how the oxidation state of multivalent cations such as  $\text{Cr}^{3+,2+}$  and  $\text{Eu}^{3+,2+}$  vary with silicate melt composition is critical to the study of magma evolution. These redox reactions permit determination of the  $f\text{O}_2$  state of the magma [1, 2] and influence the partitioning relationships between mineral and melt [3].

If we write a redox reaction in the form



where  $n$  is the number of electrons in the reduction, we see that the redox state of the cation depends on  $f\text{O}_2$ , oxide ion activity in the melt, and the activities of the cations in the melt. The activities of  $\text{O}^{2-}$ ,  $M_{(\text{Ox})}$ , and  $M_{(\text{Red})}$  can all change as the melt composition changes, resulting in changes in enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) of reaction with composition.

In attempts to simplify the complex dependence of redox state on composition, it has been suggested that  $\Delta H$  may be constant [3], that  $\Delta S$  is constant and  $\Delta H = 0$  [2], or that changes in  $\text{O}^{2-}$  activity control the change in redox state with composition [4]. Empirical models for predicting  $\text{O}^{2-}$  activity have been formulated in order to model (e.g. Eu) oxidation state as a function of composition [5]. However, separate effects of changes in activities of  $\text{O}^{2-}$ ,  $M_{(\text{Ox})}$ , and  $M_{(\text{Red})}$  can not be directly determined experimentally [6], and the simplifications above reflect in part the investigators' biases.

In this study, we attempt an indirect inference of the effects of changes with composition in  $\text{O}^{2-}$  activity relative to changes in  $M_{(\text{Ox})}$  and  $M_{(\text{Red})}$  activities by taking advantage of the observation that changes in  $\text{O}^{2-}$  activity will affect all redox reactions by the same amount. Figure 1 illustrates the change in reduction potential ( $E^* = -\Delta G^*/nF$ ) between two compositions, a diopsidic melt and a basalt-like composition in which MgO has been substituted for FeO so that electrochemical measurements can be made [7] ( $\text{SiO}_2=55.3$  wt%,  $\text{Al}_2\text{O}_3=20.2$ ,  $\text{MgO}=15.3$ ,  $\text{CaO}=9.3$ ). If  $\text{O}^{2-}$  activity were controlling the change in reduction potential for these cations, the data should fall in a horizontal line in Fig. 1. The data are significantly distant from a horizontal line, demonstrating that changes in  $\text{O}^{2-}$  activity are not the only important effects of changing composition. Activities of  $M_{(\text{Ox})}$  and  $M_{(\text{Red})}$  change as well.

Further support of this statement is seen in Table 1, reporting  $\Delta H$  and  $\Delta S$  for the reduction reactions. Similar types of reactions (In-Ni, Cr-Eu) have similar changes in  $\Delta H$  and  $\Delta S$ , suggesting the cations involved have a larger effect on the change in redox state with composition than does  $\text{O}^{2-}$  activity.

It was reported by [4] that variations in free energy for reduction of Ni can be related to changes in  $\text{O}^{2-}$  activity as modeled by the degree of melt polymerization

$$\text{O}^{2-} = K [(\text{Si-O-})^2/(\text{Si-O-Si})]. \quad (2)$$

However, the correlation they observed was for melts considerably less polymerized than those typical in nature. At higher degrees of polymerization their data leveled off or trended in the opposite direction to that expected based on the degree of polymerization.

Likewise, between the two compositions of this study, we observe that the mean change in reduction potential is opposite that expected if  $\text{O}^{2-}$  activity is determined by equation 2 and is controlling changes in Free energy of reduction (Fig. 2) (see also [8]). This paradox in silicate melts, where the change in reduction potential is opposite that expected from the change in basicity, has been noted before [6, 9].

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[9] offered the qualitative explanation for the Eu reduction that  $\text{Eu}^{2+}$  is stabilized relative to  $\text{Eu}^{3+}$  in melts enriched in plagioclase component because of the stabilizing of the  $\text{Eu}^{2+}$  in the plagioclase crystal structure (presuming the short-range melt structure to reflect in part the structure of minerals that would crystallize from it at lower temperature). Our results are consistent with this interpretation. We further suggest that our results for Cr reduction can be explained by presuming  $\text{Cr}^{3+}$  to be stabilized relative to  $\text{Cr}^{2+}$  in melts enriched in a spinel component, as  $\text{Cr}^{3+}$  is stabilized in the mineral spinel.

Although uncertainties for  $\Delta H$  and  $\Delta S$  for Eu and Cr are large (Table 1) we note that the values for  $\Delta H$  change little while values for  $\Delta S$  change by nearly a factor of two (although values are within uncertainty of each other!), again consistent with the interpretation that the change in Cr and Eu redox potentials with composition is due primarily to changes in the configurational entropy or the number of sites available in the melt, as is consistent with the interpretation above. Better values for  $\Delta S$  need to be available before this argument can be conclusive.

Acknowledgements: We thank NASA for support through UA/NASA space engineering center for utilization of local planetary resources and through grant NAGW-122.

[1] Philpotts J. A. (1970) EPSL 9, 257-268 [2] Drake M. J. (1975) GCA 39, 55-64 [3] Schreiber H. D. and Haskin L. A. (1976) Proc. Lunar Sci. Conf. 7th, 1221-1259 [4] Semkow K. W. and Haskin L. A. (1985) GCA 49, 1897-1908 [5] Lauer H. V. Jr. and Morris R. V. (1977) Jnl Am. Ceram. Soc. 60, 443-451 [6] Douglas R. W., Nath P., Paul A. (1965) Phys. Chem. Glasses 6, 216-223 [7] Colson R. O. and Haskin L. A. (1989) LPSC XX, 177-178 [8] Keedy C. R., Colson R. O., and Haskin L.A. this volume [9] Jeddloh G. (1984) Phys. Chem. Glasses 25, 163-164 [10] Schreiber H. D. (1987) J. Geophys. Res. 92, 9225-9232.

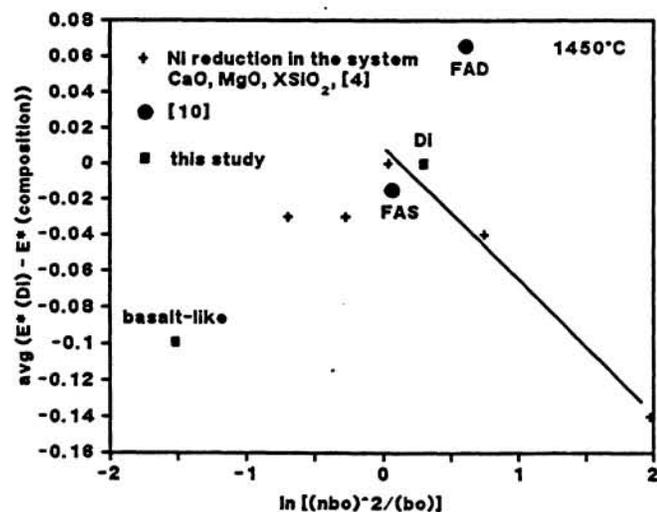


Fig. 2 dependence of reduction potential on melt polymerization. Except for the data of [4], points represent the mean change in  $E^*$  for several cations. Line indicates the change expected based on equations (1) and (2). Only at a low degree of polymerization is this line valid.  $nbo$ =non-bridging oxygen calculated from atomic fraction of ions as  $nbo=nbo'/(nbo'+bo')$ , and  $nbo' = 2 \cdot [O] - 4 \cdot [Si] - 3 \cdot [Al]$ .  $bo' = [O] - nbo'$ .

Table 1

	Basalt-like		Diopsidic	
	$\Delta H^*$	$\Delta S^*$	$\Delta H^*$	$\Delta S^*$
Cr	$34.5 \pm 13$	$9.6 \pm 7$	$28.9 \pm 3$	$6.7 \pm 2$
Ni	$31.8 \pm 12$	$10.6 \pm 7$	47.6	$17.0^1$
In	$51.0 \pm 12$	$19.5 \pm 7$	$78.3 \pm 8$	$32.6 \pm 5$
Eu	$33.4 \pm 13$	$10.3 \pm 7$	$30.7 \pm 5$	$5.3 \pm 3$

Enthalpy values in Kcal/mole

Entropy values in cal/mole: at  $\text{PO}_2=1\text{atm}$ .

<sup>1</sup> Ni Di data from [4]

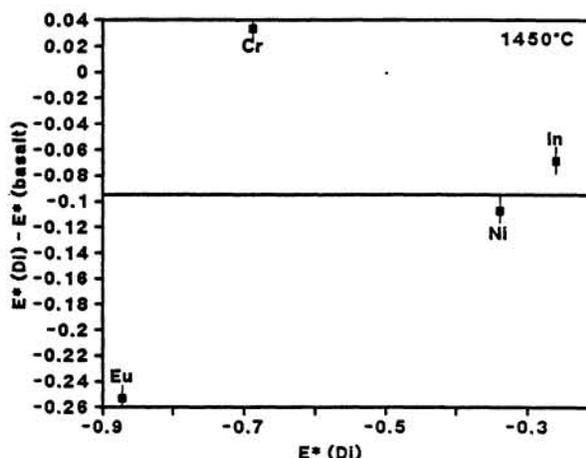


Fig. 1 Change in reduction potential for several cations between diopsidic and basalt-like melts, demonstrating that the activity of the oxide ion is not the only important composition-dependent variable.