

A STUDY OF REDOX BEHAVIOR OF NI IN SILICATE MELTS OF DIOPSIDIC TO ANORTHITIC COMPOSITION by C.R. Keedy, R.O. Colson, and L.A. Haskin Department of Earth and Planetary Sciences and McDonnell Center for Space Sciences, Washington University, St. Louis, MO 63130

In order to obtain a better understanding of the behavior of trace elements in silicate melts of geochemical interest and the nature of these melts, Stationary Electrode Polarography (SEP)[1] has been employed to study the redox behavior of the Ni²⁺ - Ni⁰ couple in a series of silicate melts ranging in composition from Diopside (CaO·MgO·2SiO₂) to Anorthite (CaO·Al₂O₃·2SiO₂) at temperatures between 1450°C and 1550°C in a CO₂ atmosphere. The MgO in diopside was incrementally substituted with the Al₂O₃ of anorthite (An_{.25}-Di_{.75}, An_{.5}-Di_{.5}, An_{.75}-Di_{.25}, Anorthite).

To confirm that the results of this study represented equilibrium conditions, we plotted peak current (i_p) in mA/cm² vs NiO concentration and i_p vs square root of the scan rate (v^{1/2}) in volts/sec and found them to be linear for diopside as well as for the other compositions, indicating a reversible, uncomplicated 2-electron process. The shapes of the polarographic curves also indicated a reversible process. The results of this work compare favorably with previous work in diopside[1]. E^{*}_{cathodic} was in agreement with previous results in diopside at .33% NiO, and the previously reported increase in E^{*} with temperature was observed here, as well.

However, E_{pk(cathodic)} was observed to shift, both as a function of concentration and of sweep rate, which is not expected for a reversible process. The previously reported E^{*}[1] was reproduced only at the reported concentration. We noted that at lower concentrations and slower scan rates, the shift in E_{pk(cathodic)} approached reversible behavior, that is the shift with scan rate disappeared and E_{pk(ca)}-E_{pk(an)} approached the theoretical value of -1.109 RT/F(see below).

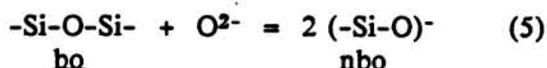
The error due to the shift with concentration can be minimized by using E^{*}_{ave} = (E^{*}_{cathodic} + E^{*}_{anodic})/2 where the E^{*}'s are calculated from the equations[2]:

$$E^*_{cathodic} = E_{pk(cathodic)} + 1.109 RT/2F + (RT/4F)\ln(f_{O_2}/f_{O_2\ air}) \quad (1)$$

$$E^*_{anodic} = E_{pk(anodic)} - 1.109 RT/2F + (RT/4F)\ln(f_{O_2}/f_{O_2\ air}) \quad (2)$$

Ideally, E^{*}_{cathodic} should approach E^{*}_{anodic} at low concentrations [3]. In these equations; R = ideal gas constant, F = Faraday constant, T = temperature in Kelvin, E_{pk} is the potential at which the current reaches its peak on the polarogram for the cathodic (reduction) and anodic (oxidation) electrode reactions of Ni, f_{O₂} is the oxygen fugacity, which was calculated from the CO₂ = CO + 1/2 O₂ equilibrium, and f_{O₂ air} is the reference state of O₂ in air at the experimental temperature [2]. Table I summarizes the E^{*}_{ave} data. This averaging process substantially, but not completely, reduced the error in the variation of the apparent E^{*} with sweep rate.

It is clear that E^{*}(Ni) increases regularly from diopside to anorthite. As the melt polymerization increases, E^{*} becomes more positive, which indicates that the Ni²⁺ ion is more easily reduced. The equations to consider are:



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Thus, according to equation 5, $[O^{2-}] = K \cdot [nbo]^2/[bo]$. A plot of E^* vs $\ln([nbo]^2/[bo])$ is shown in Figure I, where $nbo = nbo'/(nbo'+bo')$, $bo = 1 - nbo$, $nbo' = 2[O] - 4[Si] - 3[Al]$, $bo' = [O] - nbo'$, and $[]$ is the atomic fraction or number of atoms in the formula for the silicate melt. $[O^{2-}]$ should be buffered by the large concentrations of $-Si-O-Si-$ and $(-Si-O)^-$ relative to the NiO concentration of $\sim 0.2\%$. Therefore, as $[nbo]^2/[bo]$ decreases, one would expect that $[O^{2-}]$ would decrease as well (if K remains constant). In eq. 4 "NiO" represents a tightly chelated Ni-Silicate-Oxygen complex of undefined nature in the melt which, upon reduction of the Ni, "releases" an oxide ion. This idea is also expressed in [4] in which the author states: "...these differences are not due to different degrees of ionization of the oxides themselves...the differences in basic strength of oxides become apparent only in the presence of anions other than O^{2-} . And it is the ability of the cation to bind these larger anions into inactive complexes which determines the behavior of the oxide as a base." Note that according to equation 4, a decrease in $[O^{2-}]$ would allow the reduction to occur more readily and thus the reduction potential would become more positive. It should be noted, however, that when the complete cell reaction is considered that the $[O^{2-}]$ factor cancels since the reference electrode is an oxygen electrode. Another explanation is that the activity of Ni^0 is decreased (relative to that of Ni^{2+}) as the melt polymerization increases due to more favorable sites in the melt "lattice" structure for Ni^0 and hence the reduction potential becomes more positive. In Figure II $E^*(\text{diopside}) - E^*$ is plotted against $\ln([nbo]^2/[bo])$ to show that these results are in agreement with those of Colson [5] and others [6,1].

References: [1] Semkow, K.W., et al. GCA 46, 1879-1899 (1982) [2] Semkow, K.W. and Haskin, L.A. GCA 49, 1897-1908 (1985) [3] Galus, Z. Fundamentals of Electrochemical Analysis Wiley (1976) [4] Chipman, J. and Chang, L. Metals Transactions, Feb., 1949, 196 [5] Colson, R.O. and Keedy, C.R. this volume [6] Schreiber, H.D. J. Geophys. Res. 92, 9225-9232 (1987)

Table I. E^*_{ave} (mV) as a Function of Melt Composition
Diopside to Anorthite at 500 mV/sec

% Anorthite	.2%NiO	.3%NiO	.2%NiO	.3%NiO	.2%NiO	.3%NiO
	<u>$E^*(1450)$</u>	<u>$E^*(1450)$</u>	<u>$E^*(1500)$</u>	<u>$E^*(1500)$</u>	<u>$E^*(1550)$</u>	<u>$E^*(1550)$</u>
0(Diopside)	-294	-299	-277			
25	-243	-243	-222	-217	-220	-210
50	-203	-211	-194	-207	-170	-178
75	-168	-183	-164	-167	-154	-150
100(Anorthite)					-150	-152

Figure I.

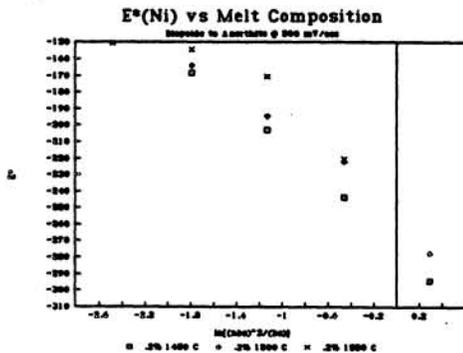


Figure II.

