

Modeling NiO Activities in Silicate Melts Considering Separate Contributions from Ni²⁺ and O²⁻: Dependence of O²⁻ on melt polymerization. L. Anderson¹, E. Young¹, and R. O. Colson^{1,2}, ¹Minnesota State University Moorhead, Moorhead MN, ²colson@mnstate.edu.

Introduction: Partition coefficients for trace element components in silicate melts depend on activity coefficients in the melt. These activity coefficients vary with composition in complex ways. We have previously proposed that modeling of trace element activities might be improved if the oxide component is modeled as the composite of separate activities for cation and oxide anion [1, 2].

Our modeling in this way has been quite successful, but we have found that a few points from the most depolymerized melts from [3] and [4] deviate from the trend of other data, suggesting unmodeled variations in depolymerized melts. We report here additional experiments in depolymerized melts to test these results and to understand what might be causing these deviations.

Experimental Methods:

End-member compositions for two series between more polymerized and less polymerized melts were prepared from reagent grade chemicals and ground with an agate mortar and pestle under methanol. These end member compositions were: Diopsidic, FMS, and SCMA10-5 (labeled as Depoly in Table 1). A series of compositions for each trend was prepared by mixing these end-member mixtures in the proportions shown in Table 1, again grinding under methanol. About 0.3wt% NiO was added to each composition.

Experiments were run on Pt wire loops in a 1-atm gas mixing furnace in a CO₂ atmosphere at temperatures as shown in Table 1. Temperatures were measured with a type-S thermocouple placed adjacent to the sample.

The activity coefficients for NiO in the Fe-free experiments were measured using square wave voltometry after the methodology in [2]. In this method, a voltage is imposed between platinum electrodes immersed in the melt and the resulting current measured. This current results from the reduction of Ni⁺² into the platinum cathode while O²⁻ is oxidized to O₂ at the anode. Free energy for the reaction, and activity coefficients for NiO, can be calculated from the voltage at which the current reaches a peak. To check for equilibrium during the experiments, we checked for shifts in peak position at different rates of voltage change.

The electrochemical method only works in Fe-free systems because reduction of the Fe would mask any current arising from the reduction of Ni²⁺. To measure the activity coefficients for NiO in the Fe-bearing systems, we used an approach similar to [5], measuring the ratio of the concentration of Ni in the Pt loop to

that in the melt (using a JEOL 733 Superprobe with long counting times). At any one temperature, pressure, and fO₂, we can compare Ni concentration in platinum in equilibrium with a known melt to that in an unknown melt according to the relationship

$$a_{\text{melt}}^*/X_{\text{Pt}}^* = a_{\text{melt}}/X_{\text{Pt}}$$

where a_{melt}^* = activity of NiO in a standard melt in which the activity coefficient is known, a_{melt} = the activity of NiO in the melt of interest, and X_{Pt} = the concentration of Ni in Pt. We calculated the activity coefficient from the relationships: $\gamma = a/X$, with the activity determined relative to the standard state of liquid NiO after the free energy expression from [3].

Table 1. Experimental Compositions and Results

	T (C)	γ NiO	SiO ₂	Al ₂ O ₃	MgO	CaO	FeO
100 % Di- Depoly	1562	1.92	55.5	0	18.6	25.9	0
75% Di- Depoly	1564	2.24	52.6	2.5	22.9	21.9	0
50% Di- Depoly	1561	2.38	49.6	5	27.3	18.0	0
35% Di- Depoly	1600	2.67	47.9	6.5	29.9	15.6	0
FMS- 75%Di	1566	1.89	49.0	0	17.7	19.4	13.9
FMS- 50% Di	1566	1.56	42.5	0	16.9	13.0	27.7
FMS- 25%Di	1564	1.33	36.0	0	16.0	6.5	41.6
FMS- 0%Di	1564	1.32	29.5	0	15.1	0	55.4

Modeling NiO Activity: Activities for NiO in silicate melts vary in a complex way with melt polymerization, as shown both by the degree of scatter in the data seen in Figure 1 and in the apparent reversal of trend.

We have proposed previously [1, 2] that in order to understand this complexity, we should look beyond NiO acting as a simple oxide compound, and instead consider the Ni⁺² cation and the O⁻² ion acting separately within the melt. The activity of NiO can be related to activities of the ionic species through a reaction of the sort NiO \leftrightarrow Ni²⁺ + O²⁻.

We have proposed [2] that a near-ideal mixing model can be derived for Ni²⁺ in silicate melts, where the Ni²⁺ mixes with a 'mixing pool' of cations of similar size and charge to Ni²⁺. The proportion of a cation

that participates in the mixing pool is inversely proportional the difference in cation size between the cation of interest and Ni^{2+} . The activity for Ni^{2+} then takes on the form of $a_{\text{Ni}^{2+}} = X_{\text{Ni}^{2+}}/\text{Mixing Pool}$.

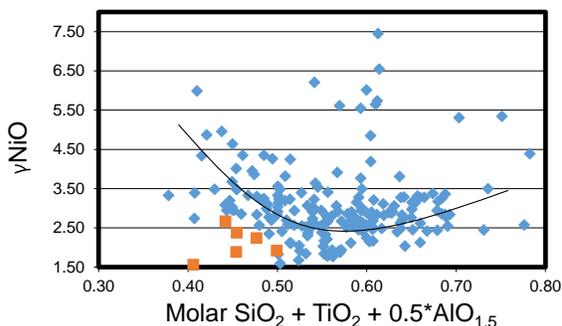
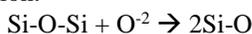
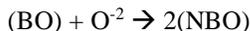


Fig. 1. NiO activity coefficients relative to a standard state of liquid NiO. Squares are from the present study. Diamonds are from [1,2,3,4,6,7,8,9,10,11,12].

We also proposed that the O^{2-} oxide ion activity can be modeled assuming that the oxide ion is buffered by bridging oxygens and non-bridging oxygens (BO and NBO respectively) according to the following reaction.



or



From this we can derive the activity of the oxide ion as the following: $a_{\text{O}^{2-}} = K(\text{NBO}^2/\text{BO})$ [2]

Figure 2 shows the residuals for this type of modeling for activity data from a number of workers. Residuals of the model are assigned to error in the modeling of the oxide ion through the expression: $0.7159 * \text{NBO}^2/\text{BO} - \gamma_{\text{NiO}}/(\text{modeled } \text{Ni}^{2+})$. Conceptually, this expression is the difference between the activity for the oxide ion modeled from the expression above and a value for the oxide ion activity based on measured values for NiO activity and the modeled Ni^{2+} activity. This yields a deviation of the modeled oxide ion activity from values based on actual measurements.

The sharp decrease in scatter in the data relative to Figure 1 shows the overall success of this approach in understanding the complex variations in NiO activity with composition, but the residuals deviate sharply from zero as the melt becomes increasingly depolymerized—meaning that our model for the activity of the oxide ion appears to become increasingly wrong for less polymerized melts. We might expect that bridging oxygens can only buffer the oxide ion under conditions where the concentration of bridging oxygens is large compared to the oxide ion, true only in highly-polymerized melts. Also, we know that the expression for the oxide ion activity above must fail at low BO, since the model predicts that the activity of

oxide ion goes to infinity as BO goes to 0, an unrealistic result. Thus, the deviation seen in Fig. 2 is not unreasonable.

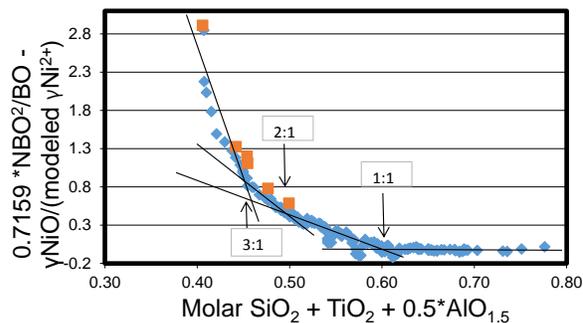


Figure 2. Data sources as in Fig 1. Ratios show ratio NBO:BO, with NBO calculated as $(2 * \text{total O}) - 4 * (\text{SiO}_2 + \text{TiO}_2 + 0.5 * \text{AlO}_{1.5}) / (\text{total O})$, and $\text{BO} = 1 - \text{NBO}$.

The activity of the oxide ion begins to deviate from the model equation at values for $\text{SiO}_2 + \text{TiO}_2 + 0.5 * \text{AlO}_{1.5}$ less than about 0.6, corresponding to a NBO/BO ratio of about 1:1. Additional sharp deviations occur at NBO/BO ratios of 2:1 and 3:1. The correlation between where these deviations occur and stoichiometric parameters for NBO/BO suggests the possibility that we can better understand variations in the oxide ion activity, and from that variations in activities for a wide range of trace element oxides, by considering that the buffering reactions controlling the oxide ion in the melt change with degree of polymerization.

Conclusions: Modeling activity for NiO by considering separate variations in activities for Ni^{2+} and O^{2-} works well, but only if the variations in activity of the oxide ion are modeled differently in regions of the melt defined by stoichiometric ratios of NBO/BO. This is consistent with the idea that fundamental reactions in the melt that buffer the oxide ion change as melt polymerization changes. Other trace oxides might be modeled in a similar fashion, with the same variation in the oxide ion applying to those components as well.

References: [1] Colson R. O., et al (1995) GCA 59, 909-925 [2] Colson R. O. et al (2005) GCA 69, 3061-3073 [3] Holzheid A. et al (1997) Chem. Geol. 139, 21-38 [4] O'Neill H St. C., and Eggins S M (2002) Chem. Geol. 186, 151-181 [5] Capobianco C J and Amelin A A (1994) GCA 58, 125-140 [6] Campbell I H and Naldrett A J (1979) Can. Mineral. 17, 495-505 [7] Doyle C D and Naldrett A J (1987) GCA 51, 213-219 [8] Ertel W et al (1997) GCA 61, 4707-4721 [9] Pretorius E B and Muan A (1992) J Am Ceramic Soc 75, 1490-1496 [10] Semkow K W and Haskin L A (1985) GCA 49, 1897-1908 [11] Snyder D A, and Carmichael I S E (1992) GCA, 56, 303-318.