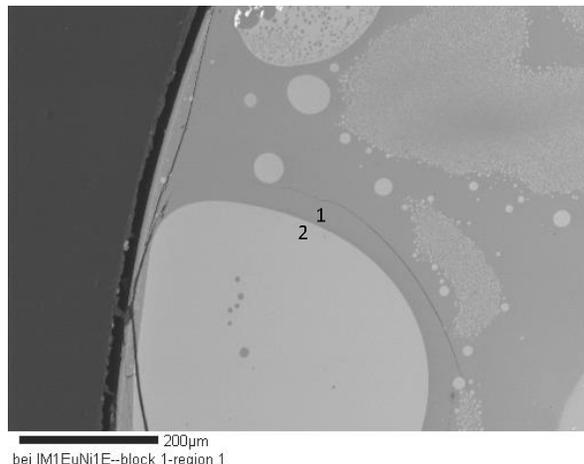


Nickel Distribution between Immiscible Melts as a Means to Understand the Influence of Ferric Iron on NiO Activity Coefficients R. O. Colson¹, E. Young, and L. Anderson,
¹Minnesota State University Moorhead, Moorhead MN 56563, colson@mnstate.edu.

Introduction: This study examines the distribution of NiO between two immiscible melts as a window into the influence of melt composition on the activity coefficient for NiO, considering the effect of ferric iron in particular. It provides theoretical constraints on modeling of activities and partitioning for trace elements in silicate melts and offers insight into the influence of ferric iron on melt structure.

Experimental Methods: Reagent grade chemicals were ground under alcohol to produce a mixture with nominal composition (wt%) of SiO₂=57.4, TiO₂=3.3, Al₂O₃=7.9, FeO (all iron)=17.1, MnO=0.25, MgO=0.45, CaO=5.6, Na₂O=1.95, K₂O=2.0 and P₂O₅=1.8. This composition was expected to produce immiscible melts based on the work of [1] and [2]. The mixed powder was fused onto a Pt wire loop and held in a Deltech gas mixing furnace in CO₂-CO gas at 1046°C for 27.7 hours. Oxygen fugacity was calculated from the proportions CO₂ and CO and the data from [3] as 2.3x10⁻⁵. Temperature was measured with a Type-S thermocouple placed adjacent to the sample.

Results: Resulting quenched glasses from immiscible melts are shown in Fig. 1. Compositions of the glasses at points 1 and 2 are given in Table 1. Molar percents are calculated from electron microprobe analysis (JEOL 733 Superprobe) and the model for ferric/ferrous ratio in [4] (making adjustments for fO₂). Differences in the concentration of NiO between the two melts can be attributed to differences in the activity coefficients for Ni²⁺.



bei IM1EuNi1E--block 1-region 1

Figure 1. Backscattered electron image of immiscible melts in experiment IM1EuNi1E—brighter phase is the more Fe and Ni-rich.

Table 1. Molar percents of the components in the immiscible phases seen in Fig. 1.

	Point 1	Point 2
	Dark phase mole percent	Light phase mole percent
SiO ₂	66.3	42.8
AlO _{1.5}	13.4	9.6
MgO	1.0	2.3
FeO	3.0	5.3
FeO _{1.5}	4.3	11.2
CaO	5.0	9.7
NaO _{0.5}	1.5	8.8
KO _{0.5}	2.9	1.2
TiO ₂	1.7	6.6
PO _{2.5}	0.52	1.94
MnO	0.26	0.28
NiO	0.08	0.23

Modeling NiO Activity: Activities for NiO in silicate melts vary with melt polymerization in complex ways. These variations can be understood as arising from covariations in activities for Ni²⁺ and O²⁻, as expected from an expression such as

$$\text{NiO} \leftrightarrow \text{Ni}^{2+} + \text{O}^{2-} \text{ [5, 6, 7].}$$

$a_{\text{Ni}^{2+}}$ can be modeled by considering that the Ni^{2+} mixes randomly (ideally) with a subset of cations in the melt (a 'mixing pool') with similar size and charge such that

$$a_{\text{Ni}^{2+}} = \frac{X_{\text{Ni}^{2+}}}{X_{\text{Ni}^{2+}} + (0.8854 \cdot X_{\text{MgO}} + 0.7641 \cdot X_{\text{CaO}} + 0.4120 \cdot X_{\text{FeO}})} \quad [7] \quad \text{Eqn. 1}$$

The activity of the oxide ion, $a_{\text{O}^{2-}}$, can be modeled by considering a reaction between bridging oxygens and non-bridging oxygens such as



From this conceptual idea, activity of the oxide ion (as it pertains to activity of NiO) can be modeled by a polynomial expression of network-forming cations in the form

$$a_{\text{O}^{2-}} = [-0.7445 + 10.4050 \cdot (\text{Oxy} - 2\text{NF}) - 30.8710 \cdot (\text{Oxy} - 2\text{NF})^2 + 33.7434 \cdot (\text{Oxy} - 2\text{NF})^3], \quad [7] \quad \text{Eqn 2.}$$

where NF= mole fraction network forming cations = $X_{\text{SiO}_2} + 0.41X_{\text{AlO}_{1.5}} + 1.75X_{\text{TiO}_2}$, and Oxy = total molar oxygens [5, 6, 7].

Discussion: Presuming that the two melts seen in Fig. 1 are in equilibrium, we can conclude the following relationships:

$$a_{\text{NiO}_{\text{phase 1}}} = a_{\text{NiO}_{\text{phase 2}}}, \quad \text{Eqn.3}$$

$$a_{\text{Ni}^{2+}_{\text{phase 1}}} = a_{\text{Ni}^{2+}_{\text{phase 2}}}, \text{ and} \quad \text{Eqn. 4}$$

$$a_{\text{O}^{2-}_{\text{phase 1}}} = a_{\text{O}^{2-}_{\text{phase 2}}} \quad \text{Eqn. 5}$$

Taking the model presented in the section above as a starting point, the equilibrium between the two melt phases places constraints on how ferric iron—a component not included in the model above—influences either Ni^{2+} activity or O^{2-} activity in the melts.

The effect of Fe^{3+} on $a_{\text{Ni}^{2+}}$ can be evaluated by adding the term $A \cdot X_{\text{FeO}_{1.5}}$ to Eqn. 1 and solving for the coefficient A through the relationship in Eqn 4. The resulting fit to the observed data are shown in Fig. 2, allowing the value of A to range between 0 (no mixing between Ni^{2+} and ferric iron) and 1 (complete mixing between Ni^{2+} and ferric iron).

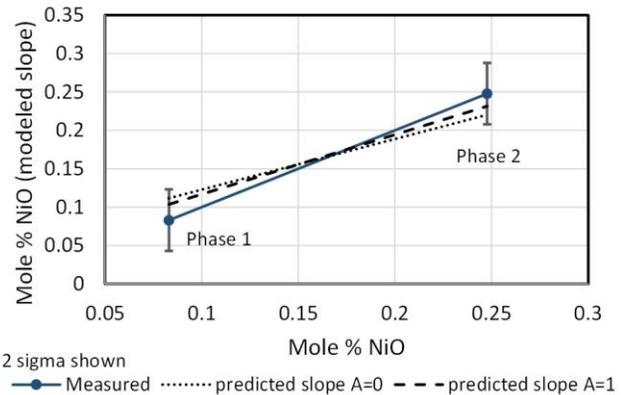


Figure 2 Comparison of observed NiO concentrations in the two immiscible melts to the slope of concentrations expected from the model in Eqn. 1, adding the term $A \cdot X_{\text{FeO}_{1.5}}$ to the denominator.

Within the uncertainty of the measurements, Eqn 1 fits the observed data regardless of the value for A, meaning that the activity of Ni^{2+} in these two immiscible melts is modeled within the uncertainty of the data by Eqn. 1 without recourse to any effect from ferric iron (although, the fit is marginally better when Ni is presumed to mix to some extent with ferric iron.)

The effect of Fe^{3+} on $a_{\text{O}^{2-}}$ can be evaluated by adding a term to the expression for network forming cations in the form of $B \cdot X_{\text{FeO}_{1.5}}$, and solving for the coefficient B through the relationship in Eqn 5 (P was assumed to act entirely as a network former). The resulting value, $B=0.9$, suggests that the ferric iron is acting mainly as a network former in the melt and its influence on the activity of NiO is mainly through its influence on $a_{\text{O}^{2-}}$. This conclusion is consistent with results reported elsewhere in this volume [8] based on a different approach.

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