

PRELIMINARY EXPERIMENTS TO CONSTRAIN THE EFFECT OF Cl ON THE ACTIVITY OF NiO IN SILICATE MELTS USING DIFFUSION PROFILES OF Ni INTO Pt WIRE LOOPS. R. O. Colson¹, Aakash BC¹, F. E. Colson,² T. Sharma¹ and Y. Kosugi¹ ¹Minnesota State University Moorhead, Moorhead MN 56563, colson@mnstate.edu, ²Florida Gulf Coast University, Fort Myers, FL 33965

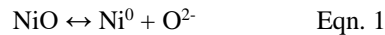
Introduction: Modeling of magmatic processes depends on understanding how the activities of melt components vary as a function of temperature, pressure, and composition. For example, we have used a model for the variation in activity of NiO and CoO in silicate melts to constrain magmatic processes on the Moon [1, 2] However, that model [1, 3, 4] does not consider any possible effect of volatiles such as Cl, S, F, CO, that may have been lost from the magmas during eruption. In the present study, we attempt to place constraints on the effect of Cl in the magma on the activities of NiO by considering the way that Ni diffuses into Pt metal as Cl is lost from the sample during experiments at 1atm pressure. Results suggest that the effect of Cl on NiO activity is less than a 2.3% change in NiO activity for each wt% Cl present.

Experimental: The silicate melt composition used in this study was of diopsidic composition but with Cl₂ substituted for 1/6th of the oxygen by combining 2 molar parts SiO₂ (added as silicic acid), one part MgO, and one part CaCl₂. About 0.2-0.5wt% of each of CoO and NiO were added to each experimental sample.

The mixture was placed on platinum wire loops and fused in a 1-atm Deltech gas mixing furnace. Experiments were conducted for 30, 45, and 90 minutes in CO₂ gas with temperatures held near 1560°C as read by a type S thermocouple. After quenching in air, samples were placed in epoxy, polished, carbon coated, and analyzed using a JEOL JXA-733 Superprobe.

Electrochemical experiments were done using the cyclic voltammetry module of a Cypress Model CS-1090 potentiostat [4], under the conditions above.

Method for deriving aNiO: NiO in the silicate melt interacts with the surface of the Pt wire loops according to the reaction



The concentration of Ni in the Pt can be related to the activity in the melt by the expression

$$(\gamma_{\text{Ni}} [\text{Ni}] [\text{O}_2]^{1/2}) / (\gamma_{\text{NiO}} [\text{NiO}]) = K_{\text{eq}} \quad \text{Eqn. 2}$$

Thus, any changes in γ_{NiO} resulting from Cl will be reflected in the concentration of Ni at the surface of the Pt wire [2, 5].

Problem of declining Cl concentration: Because Cl is volatile under our 1-atm experimental conditions, Cl is continuously lost during the experiments. Therefore the effect of Cl on NiO activity cannot be simply determined by measuring the concentration of Ni in the Pt at the end of the experiment because this value will reflect equilibration after nearly all of the Cl is lost.

The decline in Cl observed in our experiments (with some dependence on bead size) is shown in Fig. 1.

Although the surface concentration of Ni in the Pt reflects the final, low-Cl, state of the melt, information about earlier conditions in the melt when Cl was still present at significant concentrations are recorded in the diffusion profile in the Pt. In this study, we attempt to model how various changes in Ni concentration at the surface of the Pt would affect the diffusion profile and thereby place constraints on how Cl affected the activity of NiO throughout the experiment.

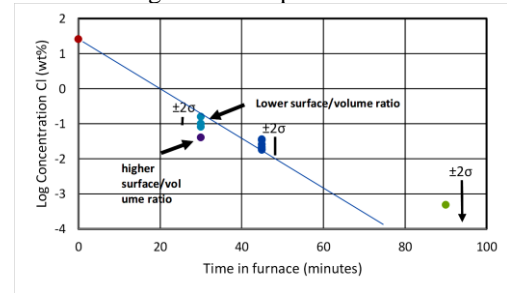


Fig. 1 Decrease in Cl concentration with time

Modeling Diffusion Profiles: We use a numerical model to compute radial concentration profiles of Ni diffusing into a wire loop using a known solution to Fick's Second Law in cylindrical coordinates. The concentration gradient in the angular and axial directions are approximated to zero, which corresponds to the majority of diffusion occurring solely in the radial direction. The concentration boundary condition at the surface of the wire loop is variable in time and the initial concentration within the wire is zero.

Fick's Second Law in cylindrical coordinates is

$$\frac{\partial C}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left(r D \frac{\partial C}{\partial r} \right),$$

where C is the volumetric weight percent of Nickel in units of $[\text{m}^{-3}]$ and D is the diffusion coefficient for Nickel through solid platinum, $5.77 \times 10^{-13} \frac{\text{m}^2}{\text{s}}$ [6]. The closed-form solution to Fick's Second Law [7] is computed using MAPLE 2019.1 where the summation is capped at $n = 100,000$:

$$C(r, t) = \frac{2D}{R} \sum_{n=1}^{\infty} \left[\frac{e^{(-D\alpha_n^2 t)} \alpha_n J_0(r\alpha_n)}{J_1(R\alpha_n)} \int_0^t e^{(D\alpha_n^2 t)} C_0(t) dt \right].$$

The minor radius is $R = 10^{-3}$ m, J are Bessel functions of the first kind of order zero and one, α_n are the roots of $J_0(R\alpha_n) = 0$, and $C_0(t)$ is the variable surface concentration function.

The variable surface concentration is the parameter of interest in this study, with three primary causes of variability 1) variations in aNiO due to the progressive loss of Cl, 2) a decline in NiO concentration in the melt with time due to loss of Ni to the Pt wire, and 3) variation in oxygen activity during the initial minutes of the experiment prior equilibration with furnace gas.

1) The variations in aNiO with Cl is the primary interest of this study. To place constraints on the maximum variation consistent with our data, we modeled the variation in aNiO as

$$\text{Percent change in aNiO} = \pm 2.3 \text{wt\% Cl, Eqn. 3}$$

For example, the presence of 2% Cl would correspond to a 4.6% increase or decrease in the activity of NiO in the melt, resulting in a similar change in the surface Ni concentration in Pt. This model is shown in Fig. 2, plotted against time rather than Cl concentration by using the relationship shown in Fig. 1.

2) Based on mass balance, the decline in NiO in the melt due to loss of Ni to Pt is expected to be low, as shown in Fig. 2. This assumes that convective mixing in the melt is fast compared to diffusion, and thus diffusion gradients in the melt are not generated.

3) Sample equilibration takes a few minutes once experiments are placed in the furnace, during which time the reaction in Eqn. 1 is shifted to the left, causing the concentration of Ni at the surface of the Pt to remain near 0. To include this effect in the diffusion model, we constrain the concentration of Ni to be 0 for the first five minutes. This is consistent with equilibration time observed in electrochemical experiments done under the same conditions (Fig. 3).

Comparing Model to Experimental Results: As seen in Fig. 4, diffusion profiles suggest that any effect of Cl falls within the limits expressed by Eqn. 3. Longer experiments become insensitive to Cl loss and so provide a test of the diffusion rate assumptions (Fig. 5).

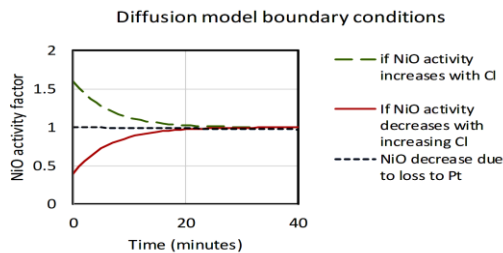


Fig. 2. Model ranges of variation in Ni concentration with time (due to Cl loss) used to place constraints on the maximum dependence of aNiO on Cl concentration.

Conclusion: Within the uncertainty of measured diffusion profiles, any effect of Cl on aNiO will be small at natural Cl concentrations (\leq Eqn. 3) and unlikely to significantly affect magma modeling of [1, 2].

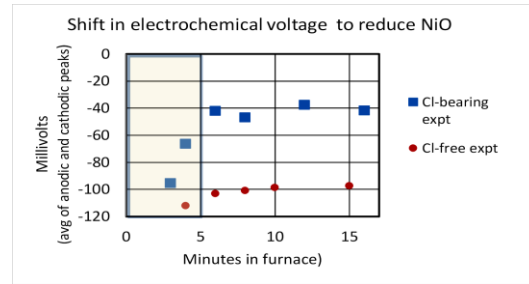


Fig. 3 Shaded region shows where experimental samples have not yet equilibrated and NiO will not reduce into Pt.

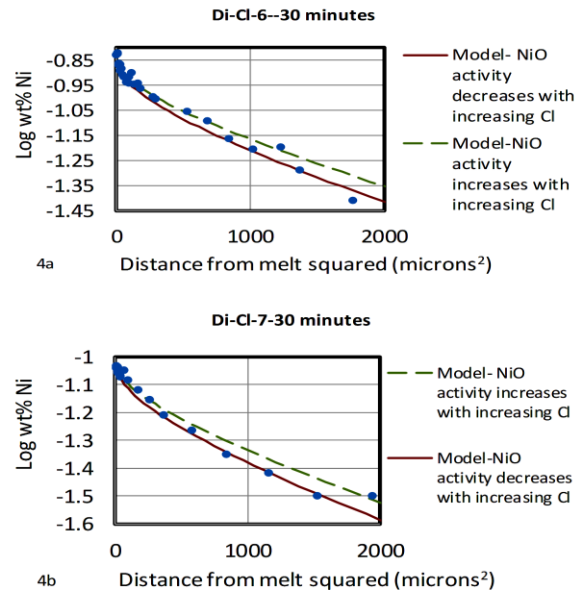


Fig. 4 Diffusion data indicate a dependence of aNiO on Cl that is less than or equal to that expressed in Eqn. 3.

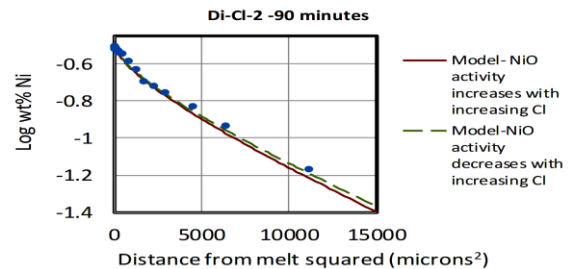


Fig. 5. Diffusion profiles become insensitive to initial Cl in longer experiments.

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