

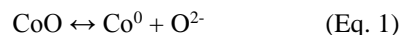
EXPERIMENTAL MEASUREMENTS OF CoO ACTIVITIES IN SILICATE MELTS. E. P. Holte¹, E. B. Dougherty¹ and R. O. Colson¹ ¹Minnesota State University Moorhead, Moorhead MN 56563, colson@mnstate.edu.

Introduction: This study looks at the activity coefficient for Cobalt in silicate melts of various compositions. Activity coefficients of trace elements in silicate melts are known to be a function of melt composition. Understanding how compositional characteristics affect activity coefficients is crucial to understanding the partitioning of trace elements into crystal phases. Previous work describing the activity coefficient of Nickel in a silicate melt offers a foundation for understanding variations observed with Cobalt.

Methods: Three series of silicate melt compositions were used in this study. One series varies from a 100% diopsidic composition (referred to as Di) to a composition more enriched in Al and Mg (referred to as SCMA10-5 abbreviated as Sc, compositionally identical to the composition called Depoly in [1]). A second series varies from 100% Di to a more polymerized composition enriched in Al (referred to as An). Table 1 shows nominal concentrations for each composition. About 0.4wt% of each of CoO and ZnO were added to each composition. The third series varies from 100% Di to an iron rich composition (referred to as FMS). This series had 0.4 wt% CoO and 0.3wt% Ni. These experiments are the same ones as were reported in [2], but we are reporting the results for Co in those experiments for the first time.

Compositions were placed on platinum wire loops and fused in a Deltech gas mixing furnace. Experiments were conducted for at least 12 hours under 1-atmosphere pressure with a constant flow of CO₂ gas and 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.

Assuming that the melt is in local chemical equilibrium with the Pt at the melt/Pt boundary, the reaction between CoO (in the melt) and Co (in the Pt) can be written as



We can use equation 1 to relate the activity coefficients for CoO (γ_{CoO}) and Co (γ_{Co}), and the concentrations [CoO] and [Co], to an equilibrium constant K_{eq}

$$[\gamma_{\text{Co}} [\text{Co}] [\text{O}_2]^{1/2}] / (\gamma_{\text{CoO}} [\text{CoO}]) = K_{\text{eq}} \quad (\text{Eq. 2})$$

Values for K_{eq} were taken from the Gibbs Free energy of formation of liquid CoO as given in [3].

We have not yet determined the value of γ_{Co} in Pt metal. We calculate an approximate value for γ_{Co} by making the assumption that the ratio of activity coefficients of CoO and NiO in one melt is approximately equal to the ratio in another melt. A ratio of the two

activity coefficients in the one melt can be found from [3] and the activity of Ni in melts of this study can be calculated from [4]. Using this method we can write

$$(\gamma_{\text{CoO}}^* / \gamma_{\text{NiO}}^*) (\gamma_{\text{NiO}}) = \gamma_{\text{Co, Pt}} \quad (\text{Eq. 3})$$

where the superscript * refers to average values from [3] for their system A, variable T, and variable fO₂. Substituting equation 3 into equation 2 for one of this study's compositions gives a working approximation for the Henry's Law activity coefficient for Co in Pt = $\gamma_{\text{Co}} \approx 0.018$.

To minimize uncertainty in our measurements for a set of experiments at any one temperature, pressure and oxygen activity, activity coefficients were normalized to that in a known diopsidic melt as was done in [2], although, for the new experiments reported in the present study, the correction was less than 2%, probably less than the uncertainty from other sources.

Table 1. Nominal molar concentrations and measured activity coefficients for compositions studied

Exp. Comp	Temp °C	γ_{CoO}	SiO ₂	CaO	MgO	AlO _{1.5}	FeO
100%Di-0%An	1554	0.83	50%	25%	25%	0.0%	0.0%
75%Di-25%An	1565	1.00	47%	24%	19%	10%	0.0%
50%Di-50%An	1571	0.94	45%	23%	12%	20%	0.0%
25%Di-75%An	1558	1.14	42%	21%	6.1%	30%	0.0%
0%Di-100%An	1550	1.28	40%	20%	0.0%	40%	0.0%
100%Di-0%Sc	1560	0.75	50%	25%	25%	0.0%	0.0%
75%Di-25%Sc	1550	0.75	46%	20%	31%	2.8%	0.0%
50%Di-50%Sc	1556	0.92	43%	16%	36%	5.3%	0.0%
25%Di-75%Sc	1565	1.06	39%	12%	41%	7.6%	0.0%
100%Di-0%FMS	1561	0.79	50%	25%	25%	0.0%	0.0%
75%Di-25%FMS	1561	0.32	45%	19%	25%	0.0%	12%
50%Di-50%FMS	1565	0.42	40%	12%	24%	0.0%	24%
25%Di-75%FMS	1562	0.35	35%	6.2%	24%	0.0%	35%
0%Di-100%FMS	1564	0.40	30%	0.0%	24%	0.0%	47%

Results and Implications: Modeled values for γ_{NiO} plotted against normalized experimental values for γ_{CoO} are shown in Figure 1. This figure shows that, to a first approximation, γ_{NiO} and γ_{CoO} are proportional to each other.

This proportionality holds true through a reversal of trend of the activity coefficient with increasing melt polymerization as shown in Figure 2. Figure 2 plots

γ_{CoO} (this study) and modeled γ_{NiO} [4] against polymerizing components SiO_2 and $\frac{1}{2} \text{AlO}_{1.5}$, showing evidence of the same reversal of trend with increasing polymerization as reported previously for NiO [5, 6, 7, 8].

Assuming the correlation between CoO and NiO observed in this study extends to other melt compositions, the activity coefficient for CoO can be modeled from Fig. 1 as a linear function of γ_{NiO} : $\gamma_{\text{CoO}} \approx 0.3\gamma_{\text{NiO}}$. γ_{NiO} can be modeled from [4], and therefore an approximation for γ_{CoO} can be modeled.

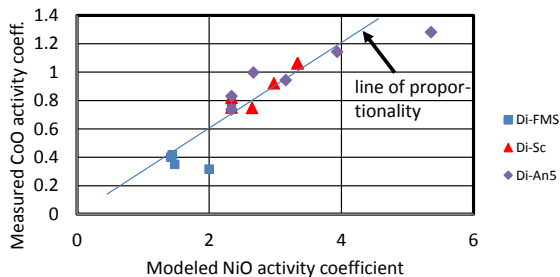


Figure 1. Measured γ_{CoO} for each composition is plotted against the modeled value for γ_{NiO} of the same composition, as calculated from [3, 4], showing a roughly proportional relationship.

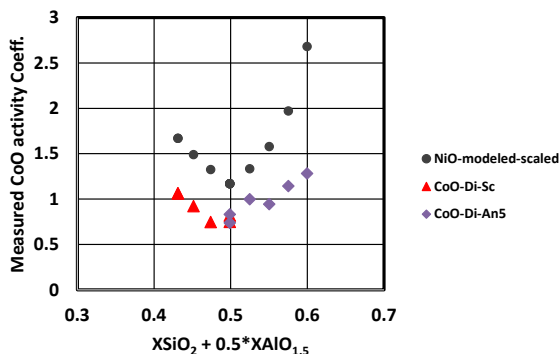


Figure 2. γ_{CoO} and modeled γ_{NiO} [4] plotted against molar concentration of SiO_2 and $\frac{1}{2}\text{AlO}_{1.5}$ showing a similar reversal of trend in the CoO activity coefficient as was reported previously for NiO.

Application to a simplified lunar problem:

Although application of these results to a crystal-melt partitioning problem requires equivalent information about activities in the crystal, the results can be more directly applied to a situation in which concentration of CoO in a melt is buffered by presence of a metal phase. Values for concentrations of both Co and Ni in olivine-normative mare basalts A15, 15016_233 and A15 15555_982 reported by [9] vary inversely with Mg#, suggesting that these two melts are not related to each other by simple fractionation or accumulation of crystal phases. However, we can ask if they might be related to each other by buffering in the presence of a metal phase. If so, then the concentration of Co in the

melt should be inversely correlated to the activity coefficient in the melt.

Variations in both Co and Ni in the two olivine-normative Apollo 15 mare basalts are consistent with control by a metal phase with constant Ni and Co activities, as shown in Fig. 3. Thus, buffering by a metal as either a residual phase in the source region or as a fractionating phase possibly explains the negative correlation between magnesium number and both Ni and Co in these two samples.

Of course, questions of this sort can't be answered without also considering other melt components and their implications for heterogeneity in the source region, assimilation during magma ascent, melt fractionation, and many other possible factors. Even so, an accurate model for CoO activities such as given in this report can provide additional constraints and insights, as those shown here.

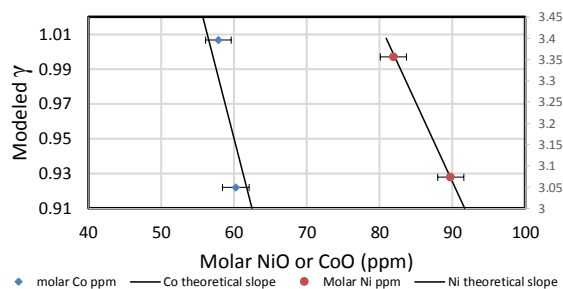


Figure 3. Molar concentrations for CoO and NiO in two mare basalts from [9], compared to the concentration expected if the melt were in equilibrium with metal at constant Ni and Co and $f\text{O}_2$ buffered parallel to Ni-NiO. Bars = 2σ .

Conclusions:

Activity coefficients for CoO in silicate melt can either increase or decrease with melt polymerization, depending on the degree of polymerization. CoO activity coefficients are well correlated with changes in γ_{NiO} . These results have implications for partitioning between silicate melts and solid phases and might be applied more directly to partitioning between silicate melt and a metal phase.

References:

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