**Introduction:** Understanding variations in activity with composition is an essential step in improving prediction of partition coefficients during magma evolution. Variations in activity with composition are complex and do not generally exhibit ideal behavior relative to a traditional melt-component set. Although deviations from component ideality can be modeled numerically by simply fitting to compositional variables (such as in a regular or subregular solution model), such models have not been particularly successful for describing variations in trace component activities. A better approach might be to try to identify components that do a better job of describing the behavior of the species in the melt.

A significant part of the nonideal contribution to activity is due not to intrinsic properties of the component in the melt, but to our ignorance about the state and mixing properties of the component in the melt. In general, the more realistically that a component’s energy state and mixing properties are portrayed, the smaller the nonideal component becomes. Looked at another way, this means that the variation in activity coefficient with composition provides insight into the mixing properties of the component in the melt.

We have measured the activity of Ru$_2$O$_3$ in a variety of melt compositions and propose that variations arise due to contributions from both $a_{\text{Ru}^{3+}}$ and $a_{\text{O}^{2-}}$ in the melt. The first of these two contributors, $a_{\text{Ru}^{3+}}$, can be understood as depending on the mixing between Ru$^{3+}$ and Al$^{3+}$, Mg$^{2+}$, and Fe$^{2+}$. Variations in the second contributor, $a_{\text{O}^{2-}}$, can be modeled by a buffering reaction with bridging and non-bridging oxygens.

### Electrochemical Measurement of Ru$_2$O$_3$ activities

Electrodes were inserted into silicate melt beads of various compositions (Table 1) suspended on Pt-wire loops in a 1-atm gas mixing furnace. An electrical potential was imposed between the electrodes, the imposed potential increasing along a step ramp with a pulse imposed on each step (Fig. 1). Current flows between electrodes when electroactive species in the melt are oxidized or reduced at the electrodes. The resulting current was measured at the top and bottom of the voltage pulse, and the difference (the differential current) was plotted against potential. The peak of the resulting curve is related to the activity coefficient for the particular electroactive species (Ru$_2$O$_3$) in the melt [1, 2, 3].

![Fig. 1 Potential step function for electrochemistry experiments.](https://ntrs.nasa.gov/search.jsp?R=20050167140)

The Ruthenium peak occurred on the shoulder of a large interfering peak associated either with oxidation of silicate melt, or oxidation of the Pt electrode; the latter being the most likely. This large peak was not very reproducible, and therefore subtracting it out as background to yield a net Ruthenium peak was not successful.

Instead, we took advantage of the observation from theoretical curves that when two different curves are added together, a sharp slope change occurs near the potential at which the two curves contribute equal amounts to the total current (Fig. 2). By averaging the $E$ value at which this slope break occurs with the $E$ value at $1/2$ that current, we derived a value for the Ru peak (Fig. 2). The resultant peak had an uncertainty of about ±14mV.

An activity coefficient (relative to a standard state of diopside melt) can be calculated from the expression:

$$\ln \gamma_{\text{melt}} = -\frac{nF}{RT}(E_{\text{pk diop}} - E_{\text{pk melt}}) + \ln[(\text{molar volume diopside melt})/(\text{molar volume melt of interest})].$$

### Table 1: Experimental compositions (wt%). 0.3wt% Ru$_2$O$_3$

<table>
<thead>
<tr>
<th></th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>MgO</th>
<th>CaO</th>
<th>run T, C</th>
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</thead>
<tbody>
<tr>
<td>diop</td>
<td>56.0</td>
<td>0.1</td>
<td>17.8</td>
<td>26.7</td>
<td></td>
</tr>
<tr>
<td>gg</td>
<td>48.4</td>
<td>8.0</td>
<td>25.7</td>
<td>16.1</td>
<td>1580</td>
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<td>gg2%Al-B</td>
<td>55.2</td>
<td>2.4</td>
<td>29.9</td>
<td>11.6</td>
<td>1578</td>
</tr>
<tr>
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<td>53.5</td>
<td>4.6</td>
<td>29.5</td>
<td>11.2</td>
<td>1587</td>
</tr>
<tr>
<td>gg10Ca-B*</td>
<td>53.3</td>
<td>9.6</td>
<td>30.5</td>
<td>6.2</td>
<td>1587</td>
</tr>
<tr>
<td>gg14Ca-B*</td>
<td>51.8</td>
<td>9.3</td>
<td>29.6</td>
<td>8.9</td>
<td>1586</td>
</tr>
<tr>
<td>gg17Mg</td>
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<td>9.4</td>
<td>16.5</td>
<td>18.6</td>
<td>1580</td>
</tr>
<tr>
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<td>8.7</td>
<td>21.2</td>
<td>17.8</td>
<td>1584</td>
</tr>
<tr>
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<td>8.3</td>
<td>27.3</td>
<td>17.7</td>
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<tr>
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<td>7.6</td>
<td>25.4</td>
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</tr>
</tbody>
</table>
Modeling activity for \( \text{RuO}_{1.5} \) and the oxide ion:

Activities of oxides in silicate melts can be understood as depending on the separate variations in activities of the cation and the oxide ion [3], after a relationship of the sort:

\[
\text{RuO}_{1.5} = \text{Ru}^{3+} + 3/2\text{O}^{2-}
\]

and

\[
\gamma_{\text{RuO}_{1.5}} = \gamma_{\text{Ru}^{3+}}(\text{O}^{2-})^{3/2}
\]

The activity of the oxide ion, \( \text{O}^{2-} \), can be considered to be buffered by reactions of the type:

\[
\text{Si-O-Si} + \text{O}^{2-} \rightarrow 2(\text{Si-O}^{-})
\]

Therefore, the activity of the oxide ion can be defined by

\[
\alpha_{\text{O}^{2-}} = K \cdot (\text{Si-O})^{3/2}/(\text{Si-O-Si})
\]

If we interpret Si-O to be non-bridging oxygens (NBO), and Si-O-Si to be bridging oxygens (BO), and define \( \alpha_{\text{O}^{2-}} \) to equal 1 in diopsidic melt, then

\[
\alpha_{\text{O}^{2-}} = 0.75 \cdot (\text{NBO})^{3/2}/(\text{BO})
\]

where NBO = \([2 \cdot \text{O} - 4 \cdot (\text{SiO}_2 + 0.5 \cdot \text{AlO}_{1.5})]/\text{O} \); BO = 1-NBO.

Inferring the mixing behavior of \( \text{Ru}^{3+} \) in silicate melts from statistical correlations:

A value for \( \gamma_{\text{Ru}^{3+}} \) can be calculated from the expression:

\[
\gamma_{\text{Ru}^{3+}} = \gamma_{\text{RuO}_{1.5}}/(\text{O}^{2-})^{3/2}
\]

Insofar as \( \text{RuO}_{1.5} \) behaves ideally relative to this proposed component set, \( \alpha_{\text{Ru}^{3+}} \propto X_{\text{Ru}^{3+}}/(\Sigma \text{ cations with which Ru}^{3+} \text{ mixes randomly}) \) and \( \gamma_{\text{Ru}^{3+}} \propto 1/(\Sigma \text{ cations with which Ru}^{3+} \text{ mixes randomly}) \).

Therefore, a regression to the expression

\[
1/\gamma_{\text{Ru}^{3+}} = A + B \cdot \text{AlO}_{1.5} + C \cdot \text{MgO} + D \cdot \text{CaO}
\]

provides an indication of the relative degree with which \( \text{Ru}^{3+} \) mixes with different cations in the melt.

The regression to 9 observations yields the following:

\[
R^2 = 0.76; \quad A = -4.57(1.09); \quad B = 4.58(2.20); \quad C = 9.27(2.03); \quad D = 12.7(2.5).
\]

For comparison purposes, an analogous regression for electrochemically derived \( \text{FeO} \) activity data (8 observations) to the expression

\[
1/\gamma_{\text{Fe}^{2+}} = A + B \cdot \text{AlO}_{1.5} + C \cdot \text{MgO} + D \cdot \text{CaO}
\]

yields the results

\[
R^2 = 0.76; \quad A = -1.67(1.41); \quad B = 0.43(2.95); \quad C = 4.64(2.11); \quad D = 5.91(3.56).
\]

The primary difference between the \( \text{Ru}^{3+} \) and \( \text{Fe}^{2+} \) results is that the \( \text{AlO}_{1.5} \) coefficient for \( \text{Ru}^{3+} \) is larger than for \( \text{Fe}^{2+} \) (relative to the other coefficients) and is more statistically significant. This is consistent with the trivalent \( \text{Ru}^{3+} \) being more likely to substitute for \( \text{Al}^{3+} \) on melt sites than is the divalent \( \text{Fe}^{2+} \). This suggests that simply assuming that network-modifiers substitute on network modifying sites and network-formers on network forming sites is inadequate.

Conclusions:

\( \text{Ru}^{3+} \) mixes on melt sites containing \( \text{Al}^{3+}, \text{Mg}^{2+}, \text{and Ca}^{2+} \). It’s mixing behavior differs from \( \text{Fe}^{2+} \), indicating that a simple model in which network-modifying cations mix equally on network modifying sites is not correct. Rather, different cations mix differently on melt sites according to their size and electrical charge. Correlations between activity coefficients and composition can provide insight into the melt components with which \( \text{Ru}^{3+} \) (or other cations) mix.

Acknowledgements:

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References:
