In our discussion of system components and phase components, it didn't really justify why we would make such choices—but often choosing the right set of phase components can significantly simplify the thermo—can make a difference between:

1) apparent non-ideal vs. ideal behavior;
2) can simplify entropy of mixing expression.

So—today let's take a trip through compositional space.

A great example is the system Fe-O in earth we usually consider two components FeO & Fe2O3. Explore consequences of this representation.

<table>
<thead>
<tr>
<th>FeO</th>
<th>0.5</th>
<th>Fe2O3</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Fe2O4</td>
<td>1</td>
</tr>
</tbody>
</table>
so where does O plot on this representation?

\[ 0 = \text{Fe}_2\text{O}_3 - 2\text{FeO} \]

\[ x_{\text{Fe}_2\text{O}_3} = \frac{n_{\text{Fe}_2\text{O}_3}}{n_{\text{FeO}} + n_{\text{Fe}_2\text{O}_3}} \]

\[ \frac{1}{-2 + 4} = \frac{n}{-4} = -\frac{1}{4} \]

how about Fe

\[ \text{Fe} = 3\text{FeO} - \text{Fe}_2\text{O}_3 = \]

\[ -\frac{1}{3 - 1} = -\frac{1}{2} \]

how about

\[ \text{FeO}_2 = \text{Fe}_2\text{O}_3 - \text{FeO} = \]

\[ \frac{1}{1 - 1} = 0 \]

how about \( \text{FeO}_3 \)

\[ \frac{2}{2 - 3} = -2 \]

so let's look at how we have divided up space

dashed line

\[ \text{Fe}_2\text{O}_3 \quad 0 \quad \text{Fe} \quad 0 \quad \frac{1}{2} \text{FeO} \quad \frac{1}{2} \text{Fe}_2\text{O}_3 \quad \rightarrow \infty \text{FeO}_2 \]

this is physically inaccessible space

is it really? let's take \( x_{\text{Fe}_2\text{O}_3} = -\frac{3}{8} \text{FeO} = \frac{3}{8} - \frac{3}{5} \)

\[ \text{Fe}_2\text{O}_3 \quad 0 \quad \text{Fe} \quad 0 \quad \frac{1}{2} \text{FeO} \quad \frac{1}{2} \text{Fe}_2\text{O}_3 \quad \rightarrow \infty \text{FeO}_2 \]
so a more normal way of representing Fe-O might be to use Fe and O as end points - then physically inaccessible space plots on either side of the line.

\[ Fe \quad \frac{3}{4} \quad x \quad Fe_2O_4 \quad 2Fe - 10 \]

in this case

\[ x = \frac{-1}{2 - 1} = -1 \]

phys. inaccessible space.

in general - represent components requires 2 choices 1) two discrete end members 2) choice of units

units should be conservative - volume is not...

atoms or mass - oxygen units is one interesting choice - normalize to the number of O's in each component

\[ Fe_3O_4 = FeO + Fe_2O_3 \]

with FeO & Fe_2O_3 as components

\[ Fe_3O_4 = \frac{3}{3+1} = \frac{3}{4} \]

this method is useful in petrology because it
can give you an idea of the volumes of phases in
we've considered a linear system of
two components - now let's go to a
representative similar to one that you've
seen us use before - e.g. ternary
in triangular space.
△ - an equilateral triangle is often used -
so let's go back to our components
FeO & Fe₂O₃ and add - SiO₂ ...

where does Si plot?

What plots at
infinity along SiO₂ - Si line?
= SiO₃

\[ \frac{x_{FeO}}{x_{Fe₂O₃}} = \frac{-2}{1 + 4 - 2} = - \frac{2}{3} \]

\[ x_{SiO₂} = \frac{4}{3} \]

\[ x_{FeO} = \frac{4}{3} \]

\[ x_{Fe₂O₃} = \frac{1}{3} \]
So how is this composition space divided up?

This oxygen representation introduces a split in composition space.

How it is supposed we choose FeO, Fe2O3 and SiO2 as components, but we use oxygen units as the reference units.

\[
\begin{align*}
\mathrm{Si} &= \mathrm{SiO}_2 + 4 \mathrm{FeO} - 6 \mathrm{Fe}_2O_3 \\
x_{\mathrm{Fe}_2O_3} &= \frac{-6}{(4+2) \times 6} = \frac{\frac{1}{3}}{12} \\
x_{\mathrm{SiO}_2} &= \frac{2}{12} \\
x_{\mathrm{FeO}} &= \frac{4}{12}
\end{align*}
\]

So here is another interesting consequence of a choice of units — take system SiO2, FeO, MgO — plot up clinopyroxene and pyroxene.

\[
\text{MgO} = \left\{ \begin{array}{l}
\text{FeO} : \text{MgO} = 1 : 1 \\
\text{FeO : MgO} = -1 : 1
\end{array} \right.
\]
If the point $\text{Form-1}$ is at infinity, what happens when we look at it with a weight units representation?

\[
\frac{X_{\text{FeO}}}{(\text{Form-1})} = \frac{71.846}{71.346 - 40.311} = 2.25
\]

\[
X_{\text{mgo}} = \frac{40}{40.160} = 0.9
\]

\[
X_{\text{mgo}} = \frac{60}{140} = 0.5
\]

\[
X_{\text{FeO} \cdot \text{SiO}_2} = \frac{72}{72 + 160} = 0.33
\]

\[
X_{\text{FeO} \cdot \text{SiO}_2} = \frac{194}{194 + 160} = 0.49
\]

One can visualize the relationship of two types of weighting schemes by selecting one component as a reference point. Let's take FeO - Fe$_2$O$_3$ and select FeO as the reference point. For example, let's use atom mole units.

\[
\text{at FeO, we will be in the mole units line and will intersect it at infinity, negative part of the project will be reversed.}
\]

\[
\text{atom units}
\]

\[
\text{Fe}_2 = \frac{-5}{-5 + 6} = \frac{-5}{1}
\]

\[
\text{mole units}
\]

\[
O = \frac{-5}{-5 + 4} = \frac{-5}{1}
\]

\[
2\text{Fe}_2\text{O}_3\]
In the case of a triangle being split into a visualization with circular space, one can use a visualization with circular space to be represented.

Ellipses, one gets either an ellipse on a parabola or hyperbola as plane of projection changes relation's sphere.

Split triangle = hyperbola

Useful to transform given one representative to another - most common in earth sci. is to be given a set of oxide components in chemical analysis.
another wrinkle in choosing components is whether or not you have encompassed all of the appropriate space. Let's say we choose 3 components, we make NaCl by reacting Na₂O with Cl₂O⁻¹. So, accessible space here is not triangular... we can represent then as a rectangle or quadrilateral However - we could pack a 3rd composite cell make the space triangular if we place Cl₂O⁻¹ at infinity we get a square.

An additional issue is what are the number of components in the system. For example - the choice above is a sub-system in the 4 component system H-Na-Cl-O.
other tricks - convenient representations in a ternary system. The corners placed at infinity.

\[ \begin{array}{c}
  A \\
  B \\
  C
\end{array} \]

useful to transform from one representation scheme to another.

-most common in earth sciences to be given a set of components of chemical analysis -

-can usually write transformation of components in a way that allows

you to invert transformation matrix easily.
the trick is to order the new components (mineral units, rows) so that the oxides (columns) containing only 1 oxide unit appear at the top of the matrix. Follow that by expressions that contain more than one oxide.

This arrangement facilitates solution of the matrix by Gaussian elimination. Gaussian elimination involves subtracting successive rows until only the leading diagonal contains non-zero terms. A lower triangular matrix can be inverted by subtracting overlying rows from underlying rows.
\[ \begin{align*}
\text{Na}_2\text{O} & : \quad \frac{1}{5} \\
\text{Al}_2\text{O}_3 & : \quad \frac{1}{5} \quad \frac{2}{5} \\
\text{SiO}_2 & : \quad \frac{3}{5} \quad \frac{2}{5} \quad \frac{1}{2} \quad \frac{1}{3} \quad 1 \\
\text{CaO} & : \quad \frac{1}{4} \\
\text{FM} & : \quad 0 \quad 0 \quad \frac{1}{4} \quad \frac{2}{3} \\
\text{Ab} & : \quad \text{An} \quad \text{Di} \quad \text{Ol} \quad \text{Qtz}
\end{align*} \]
\[ Al_0 = Na_0.5 \]

\[ An = \frac{-Na_0.5 + AlO_1.5}{2} \]

\[ D_i = \frac{Na_0.5 - AlO_1.5 + CaO}{2} \]

\[ O_i = \frac{-Na_0.5 + AlO_1.5 - CaO}{2} + \frac{FM}{2} \]

\[ Qtz = -2\frac{3}{4} Na_0.5 - \frac{AlO_1.5}{4} - \frac{3}{2} CaO - \frac{FM}{2} + SiO_2 \]

\[ Sum = -2 Na_0.5 - 0 - CaO - 0 + SiO_2 \]
Botinga and Weil restrict their model to *geologically-relevant* melts. Since for most melts, $M_{2}O + M_{2}O > Al_{2}O_{3}$, most of the $Al_{2}O_{3}$ will be in tetrahedral coordination (complexes with $Al$ and $O$ can form). Thus Botinga and Weil express the composition of silicate melt in terms of the following simple components:

$$KAl_{2}O_{2}, NaAl_{2}O_{2}, CaAl_{2}O_{4}, MgAl_{2}O_{4}, SiO_{2}, TiO_{2}, FeO, MgO, CaO, Na_{2}O, K_{2}O$$

To calculate these components one combines $K_{2}O$ and $Na_{2}O$ with $Al_{2}O_{3}$, then with $Ba, Sr, Ca, Mg, Mn$ in order until all of the $Al_{2}O_{3}$ is used up. In other words, the power of the oxides to make complexes with $Al$ is (from highest propensity to lowest propensity to make complexes with $Al$):

$$K_{2}O \rightarrow Na_{2}O \rightarrow BaO \rightarrow SrO \rightarrow CaO \rightarrow MgO \rightarrow MnO$$

This model has been used by Drake and others to calculate an activity based on the presence of a network former amongst other similar structural units.

For example,

$$a_{SiO_{2}} = \frac{X_{SiO_{2}}}{X_{SiO_{2}} + X_{NaO_{0.5}} + X_{K0.5}}$$

where the denominator is the mole-fraction of network-forming cations; similarly,

$$a_{MgO} = \frac{X_{MgO}}{X_{MgO} + X_{FeO} + X_{CaO} + X_{TiO_{2}} + (X_{AlO_{0.5}} - X_{NaO_{0.5}} - X_{K0.5})}$$

where the denominator is the mole-fraction of network-modifying cations.