representation of composition space

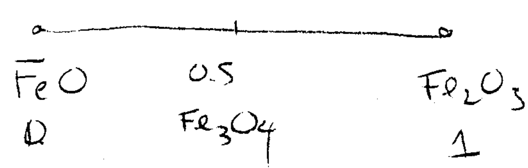
→ in our discussion of system components & phase components - didn't really justify why we would make such choices - but often choosing the right set of phase components can significantly simplify the thermo - can make difference between
(1) apparent non-ideal vs. ideal behavior -
(2) can simplify entropy of mixing expressions

so - today let's take a trip through composition space.

great example is the system Fe-O

in earth we usually consider 2 components FeO & Fe_2O_3

explore consequences of this representation



so, where does O plot on this representation?

$$O = Fe_2O_3 - 2\,FeO \qquad X_{Fe_2O_3} = \frac{n_{Fe_2O_3}}{n_{FeO} + n_{Fe_2O_3}}$$

$$\frac{1}{-2+1} = \frac{1}{-1} = -1$$

how about Fe

$$Fe = 3FeO - Fe_2O_3 =$$

$$\frac{-1}{3-1} = -\frac{1}{2}$$

how about

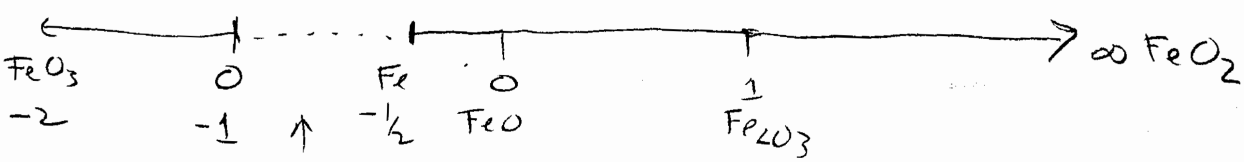
$$FeO_2 = Fe_2O_3 - FeO =$$

$$\frac{1}{1-1} = \infty$$

how about FeO_3

$$= \frac{2}{2-3} = -2$$

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



this is physically inaccessible space

is it really? let's take Fe_2O_{-1} $= \begin{matrix} 8FeO \\ -3Fe_2O_3 \end{matrix} = \frac{-3}{8-3} = \frac{-3}{5}$

yep

so – a more normal way of representing Fe-O might be to use Fe and O as endpoints – then physically inaccessible space plots on either side of the line

outside of phys. accessible space.

in this case

$Fe_2O_{-1} = 2Fe - 1O$

$$X_0 = \frac{-1}{2-1} = -1$$

in general – representing 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

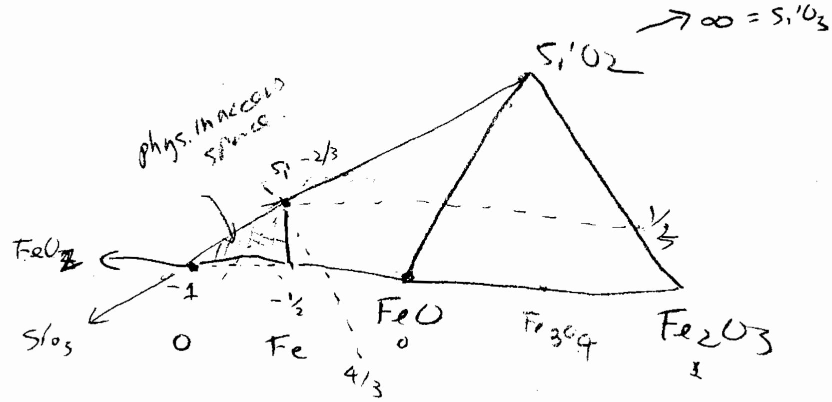
in oxygen units with FeO & Fe_2O_3 as components

$$Fe_3O_4 = FeO + Fe_2O_3 = \frac{3}{3+1} = \frac{3}{4}$$

this method is useful in petrology because it can give you an idea of the volumes of phases ~~$M~~

we've considered a linear system of two components - now let's go to a representation similar to one that you've seen us use before - e.g. ternary or triangular space.

△ - an equilateral triangle is often used - so let's go back to our components FeO & Fe_2O_3 and add - SiO_2 ...



where does Si plot?

$Si = SiO_2 + 4FeO - 2Fe_2O_3$

$X_{Fe_2O_3} = \frac{-2}{1+4-2} = -\frac{2}{3}$

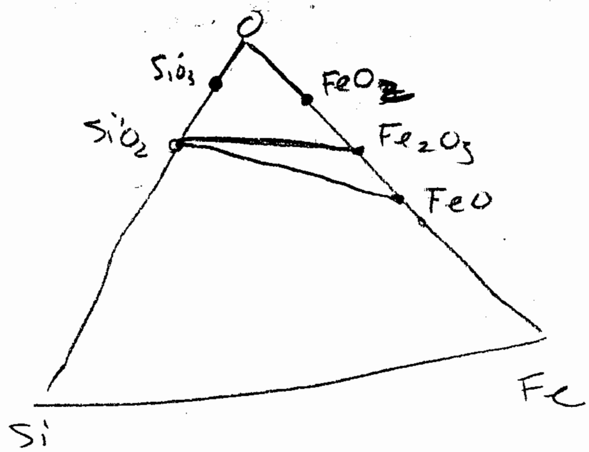
$X_{SiO_2} = \frac{1}{3} =$

$X_{FeO} = \frac{4}{3}$

$\Sigma = \overline{\quad 1}$

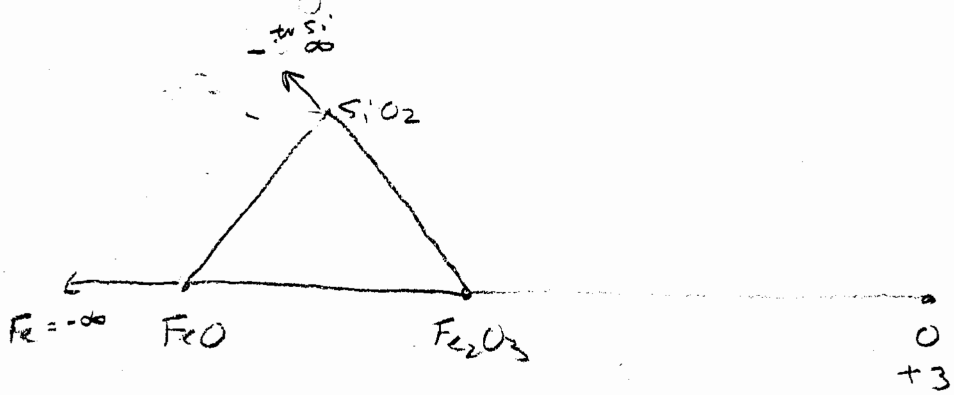
what plots at infinity along SiO_2-Si line?
$= SiO_3$

So now how is composition space divided up? (5)



This oxygen representation introduces a split in composition space.

now let's suppose we choose FeO, Fe_2O_3 and SiO_2 as components BUT we use oxygen units as the reference units



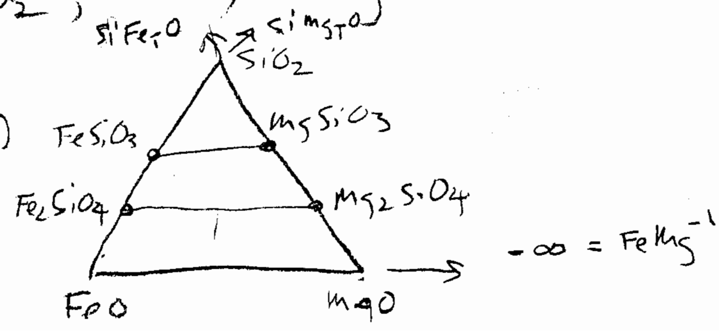
$Si = SiO_2 + 4FeO - 6Fe_2O_3$

$X_{Fe_2O_3} = \frac{-6}{(4+2)-6} = \frac{-1}{0} = -\infty$

$X_{SiO_2} = \frac{2}{12}$

$X_{FeO} = \frac{4}{12} =$

so here is another interesting consequence of a choice of units — take system SiO_2, FeO, MgO — plotting olivines and pyroxenes



$FeMg^{-1}$

in terms of components = $FeO - MgO$

$\frac{-1}{1-1} = -\frac{1}{0}$

Is the point FeMg-1 is at infinity - ~~what~~ happens ⑥
when we look at it with a weight units, representation.

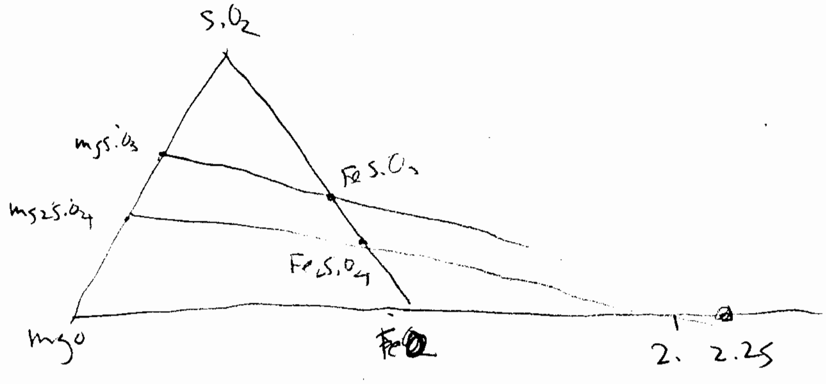
$$X_{FeO\,(FeMg^{-1})} = \frac{71.846}{71.846 - 40.311} = \sim 2.25$$

$$X_{MgO}^{MgSiO_3} = \frac{40}{40+60} = 0.4$$

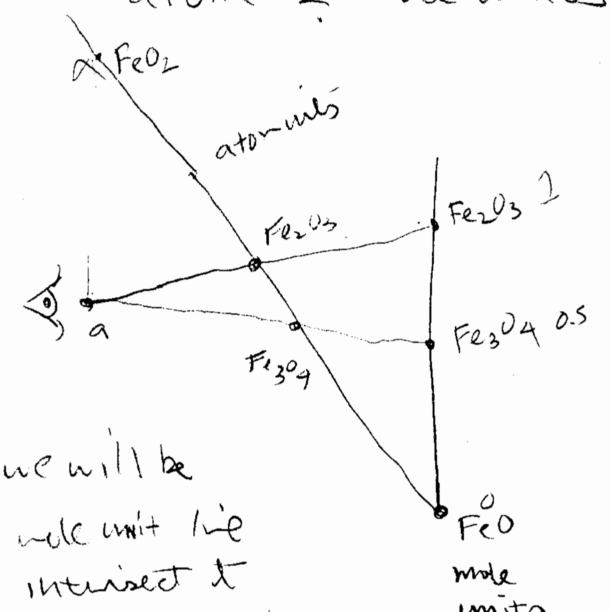
$$X_{MgO}^{Mg_2SiO_4} = \frac{80}{140} = 0.57$$

$$X_{FeO}^{FeSiO_3} = \frac{72}{72+60} = 0.54$$

$$X_{FeO}^{Fe_2SiO_4} = \frac{144}{144+60} = 0.70$$



one can visualize the relationship of 2 types of weighting schemes by selecting one component as a reference point
let's take FeO - Fe_2O_3 and select FeO as the reference point. ~~for the~~ example - let's use atom & mole units



atom units

FeO_2 in atom units $= \frac{5}{5-2} = \frac{5}{3}$

$Fe = \frac{-5}{-5+6} = \frac{-5}{1} = -5$ ($3FeO - Fe_2O_3$)

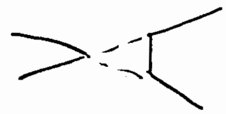
$O = \frac{-5}{-5+4} = 5$

($2FeO - Fe_2O_3$)

at FeO_2 we will be ∥ to the mole unit line and will intersect it at infinity. negative part of the projection will be reversed.

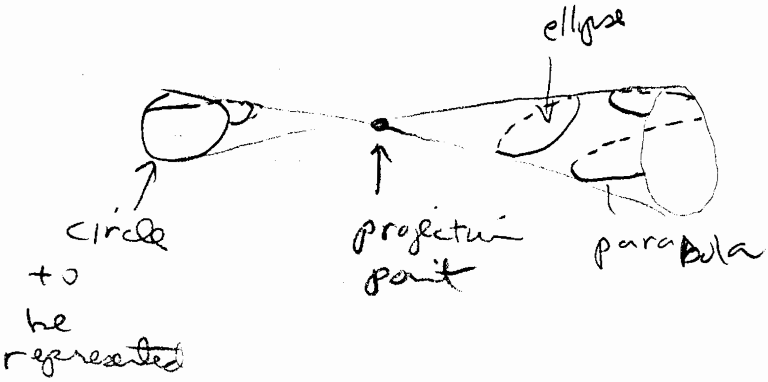
This is just another way of visualizing how projective ... projected position in the case of a triangle being split into

like so....



one can use a visualization with circular

space



one gets either an
ellipse or a parabola
or hyperbola
as plane of projection
changes relationships

split triangle ~ hyperbola

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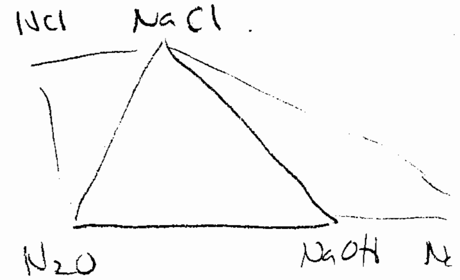
useful to transform from one representation
to another - most common in earth sci. is to
to be given a set of oxide components - a chemical
analysis.

save
for later

another <u>wrinkle</u> in choosing components is whether or not you have encompassed all of the appropriate space.

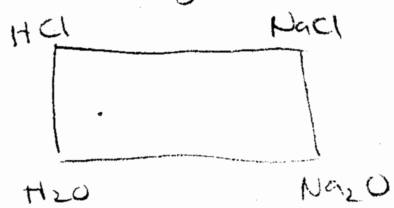
let's say we choose 3 components



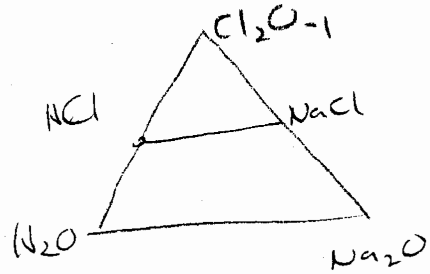
we make HCl by removing

Na_2O

So - accessible space here is not triangular..... we can represent them as a rectangle or quadrilateral

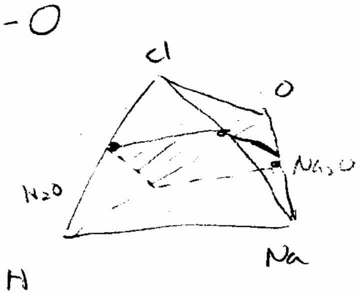


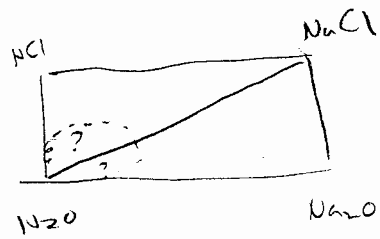
However - we could pick a 3rd composition and make the space triangular



if we place Cl_2O_{-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

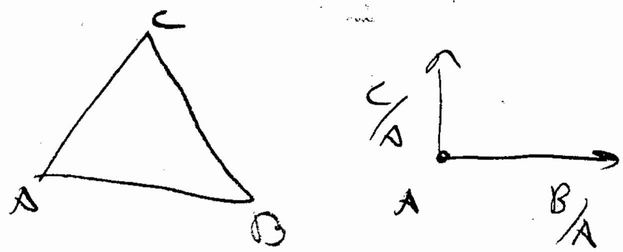




water is a phase region of this diagram

1.
2. we don't

other tricks – convenient representations in a ternary system are if the corners can be placed at infinity



useful to transform from one representation scheme to another

- most common in earth sciences to be given a set of oxide components a 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 ~~n~~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

(inversion)
this arrangement facilitates solution of the matrix by Gaussian elimination.

- Gaussian elimination involves subtraction of 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.

$Na_2O\,Al_2O_3\,6SiO_2$

$NaAlSi_3O_8$

$NaO_{.5}$ Na_2O

$AlO_{1.5}$ Al_2O_3

$3SiO_2$ $6SiO_2$

CaO

$2\,AlO_{1.5}$

$2\,SiO_2$

		Ab	An	~~Di~~	Ol	Qtz
$NaO_{.5}$	=	1/5				
$AlO_{1.5}$	=	1/5	2/5			
CaO	=	0	1/5	1/4		
FM	=	0	0	1/4	2/3	
SiO_2	=	3/5	2/5	1/2	1/3	1

	Ab	An	Di	Ol	Qtz
$+NaO_{.5} =$	1/5				
$+\frac{AlO_{1.5}}{2} - \frac{NaO_{.5}}{2} =$		2/5			
$CaO - \frac{AlO_{1.5}}{2} + \frac{NaO_{.5}}{2} =$			1/4		
$\frac{FM}{2} - \frac{CaO}{2} + \frac{AlO_{1.5}}{4} - \frac{NaO_{.5}}{4} =$				2/3	
$SiO_2 - \frac{FM}{2} + \frac{CaO}{2} - \frac{AlO_{1.5}}{4} + \frac{NaO_{.5}}{4} =$					1

$-2CaO \quad +AlO_{1.5} \quad -NaO_{.5}$

$-AlO_{1.5} \quad +NaO_{.5}$

$-3NaO_{.5}$

$SiO_2 - \frac{FM}{[\text{cut off}]} - 3/4\,CaO - AlO_{1.5} - 2\,3/4\,NaO_{.5}$

$$Ab = NaO_{.5}$$

$$An = -\frac{NaO_{.5}}{2} + \frac{AlO_{1.5}}{2}$$

$$Di = +\frac{NaO_{.5}}{2} - \frac{AlO_{1.5}}{2} + CaO$$

$$Ol = -\frac{NaO_{.5}}{4} + \frac{AlO_{1.5}}{4} - \frac{CaO}{2} + \frac{Fm}{2}$$

$$Qtz = -2\tfrac{3}{4}\,NaO_{.5} - \frac{AlO_{1.5}}{4} - \tfrac{3}{2}CaO - \frac{Fm}{2} + SiO_2$$

$$Sum = -2\,NaO_{.5} \quad 0 \quad -CaO \quad 0 \quad SiO_2$$

Botinga and Weil restrict their model to geologically-relevant melts. Since for most melts, $MO + M_2O >> Al_2O_3$, most of the Al_2O_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:

$KAlO_2$, $NaAlO_2$, $CaAl_2O_4$, $MgAl_2O_4$, SiO_2, TiO_2, FeO, MgO, CaO, Na_2O, K_2O

To calculate these components one combines K_2O and Na_2O with Al_2O_3, then with Ba, Sr, Ca, Mg, Mn in order until all of the Al_2O_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):

$K_2O \rightarrow Na_2O \rightarrow BaO \rightarrow SrO \rightarrow CaO \rightarrow MgO \rightarrow MnO$

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,

$$a_{SiO2} = \frac{X_{SiO2}}{XSiO2 + X_{NaO0.5} + X_{KO0.5}}$$

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

$$a_{MgO} = \frac{X_{MgO}}{X_{MgO} + X_{FeO} + X_{CaO} + X_{TiO2} + (X_{AlO0.5} - X_{NaO0.5} - X_{KO.5})}$$

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