Seminar 1

The objective of the seminar phase of this course is for students to read and understand important papers published in the field of Trace Element Geochemistry. Initially seminars are between lectures but eventually the course evolves to a series of seminars focused on papers that use Trace Element Geochemistry to address the petrogenesis of igneous rocks.

Each student must read the selected paper carefully; typically at least two readings, and then interact orally in class discussion on the pros and cons of the paper.

For the Web-based version of the course I list a series of questions and comments that the student should understand.

The first seminar paper is "The importance of melt composition in controlling trace-element behaviour: an experimental study of Mn and Zn partitioning between forsterite and silicate melt" by Kohn and Schofield, Chemical Geology, 17, 73-87, 1994.

Discussion Points:

1) Why study these elements in the simple system Fo-Ab-An? (see page 74).

2) An important aspect of any experimental study is an evaluation if equilibrium was attained (see Figure 1). What is a "reversal" (see page 76).

3) If the concentration of the trace element is high, well above that found in natural systems, in order to enable accurate measurements in all phases being studied, it is essential to evaluate if Henry's Law is obeyed (see p. 76).

4) How is Figure 2 useful? In particular, if you connect for each experiment the bulk composition and glass composition, what do you learn?

5) The most important point of the paper is that NBO/T (the number of non-bridging oxygens per tetrahedral cation) is a useful parameter that reflects the extent of polymerization of a silicate melt; NBO/T = 0 represents a fully polymerized melt and NBO/T = 4 is a fully depolymerized melt consistent of isolated tetrahedra.

(a) Note how $D_{Mn}^{Fo/melt}$ varies with NBO/T (Figure 3).

(b) Understand why NBO/T is preferred to Si/O (Watson, 1977). See figure 5, compare Si/O and NBO/T for Fo and Ab. Why do they differ?

(c) Calculate NBO/T for several glass compositions in Table 3. Can you reproduce the values in this table?

To assist your understanding the following example is adapted from Drake and Weill, Geochim. Cosmochim. Acta, 39, 689-712, 1975.

Consider the formation of anorthite feldspar from a liquid, i.e.

$MO(\ell) + Al_2O_3(\ell) + 2SiO_2(\ell) = MAl_2Si_2O_8(s)$. For pure anorthite $M^{+2} = Ca^{+2}$ and the equilibrium constant can be expressed in terms of activities, i.e.

$$K_{Eq} = \frac{(MAl_2Si_2O_8)_s}{(MO)_\ell (Al_2O_3)_\ell (SiO_2)_\ell^2}$$

We want to estimate values for activities. For the melt (ℓ) a useful approximation is a two lattice model for melt structure, i.e., silicate melt, can be considered as consisting of network formers and modifiers. For example, the melt can be considered in terms of two distinct types of components, those associated with the formation of TO_4 tetrahedral polymerizing units (network-forming components), and components which tend to weaken or disrupt the T-O-T bonds between polymerized tetrahedral units (network-modifying

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components). In magmatic liquids saturated with plagioclase the important network-forming components are SiO_4, $KA1O_2$, $NaAlO_2$, $BaAl_2O_4$, $SrAl_2O_4$ and $CaAl_2O_4$ and the network-modifying components are CaO, MgO and FeO. The $MA1O_3$ and MAl_2O_4 components essentially reflect the well-known tendency of cations like K^+, Na^+, Ba^{2+}, Sr^{2+} and Ca^{3+} to be associated with AlO_4 tetrahedral units in igneous minerals. Furthermore, melt viscosity data (Bottinga and Weill, 1972) indicate that the addition of these components increases viscosity in the order $KAlO_2 > NaAlO_2 > BaAl_2O_4 > SrAl_2O_4 > CaAl_2O_4$; hence this order may be taken as an indication of the relative affinity of the large cations to associate with tetrahedral Al in the melt. Accordingly, the bulk composition of the liquids may be expressed in terms of molar concentrations of network-forming and network-modifying components, calculating the $MAlO_2$ and MAl_2O_4 components in the order given above. Petrologists will recognize in this procedure certain similarities to normative calculations.

In applying this approach we can express K_{Eq} as:

$$K_{Eq} = \frac{[MAl_2Si_2O_8]_s}{[MAl_2O_4]_l[SiO_2]_l^2} \; .$$

The network-forming and network-modifying components are considered to occupy non-equivalent positions in the liquid structure, but as a first approximation we consider that random mixing occurs among like components. The entropy of ideal mixing on the two separate quasi-lattices gives us approximations to the activities.

$$[MAl_2O_4] = (MAl_2O_4)/(\Sigma \text{ network-forming components})$$

and

$$[SiO_2] = (SiO_2)/(\Sigma \text{ network-forming components})$$

The terms in parentheses refer to mole fractions. For the calculation, you need to convert wt.% to mole %, assume only Si and Al are in tetrahedral coordination (i.e. network forming) but that for charge balance you must combine Al with Na and Ca to form $NaAlO_2$ and $CaAl_2O_4$.

We assume that M^{2+} occupies large-cation lattice positions rather than defect sites in plagioclase. Assuming ideal solid solution at high temperature, the activity of $MAl_2Si_2O_8$ in the solid is approximated by $(M)/(\Sigma M+Na+Ca)$.

6) What are the significant implications arising from this paper for using Trace Element Geochemistry to understand the petrogenesis of basic (mafic) and acidic (silicic) rocks?