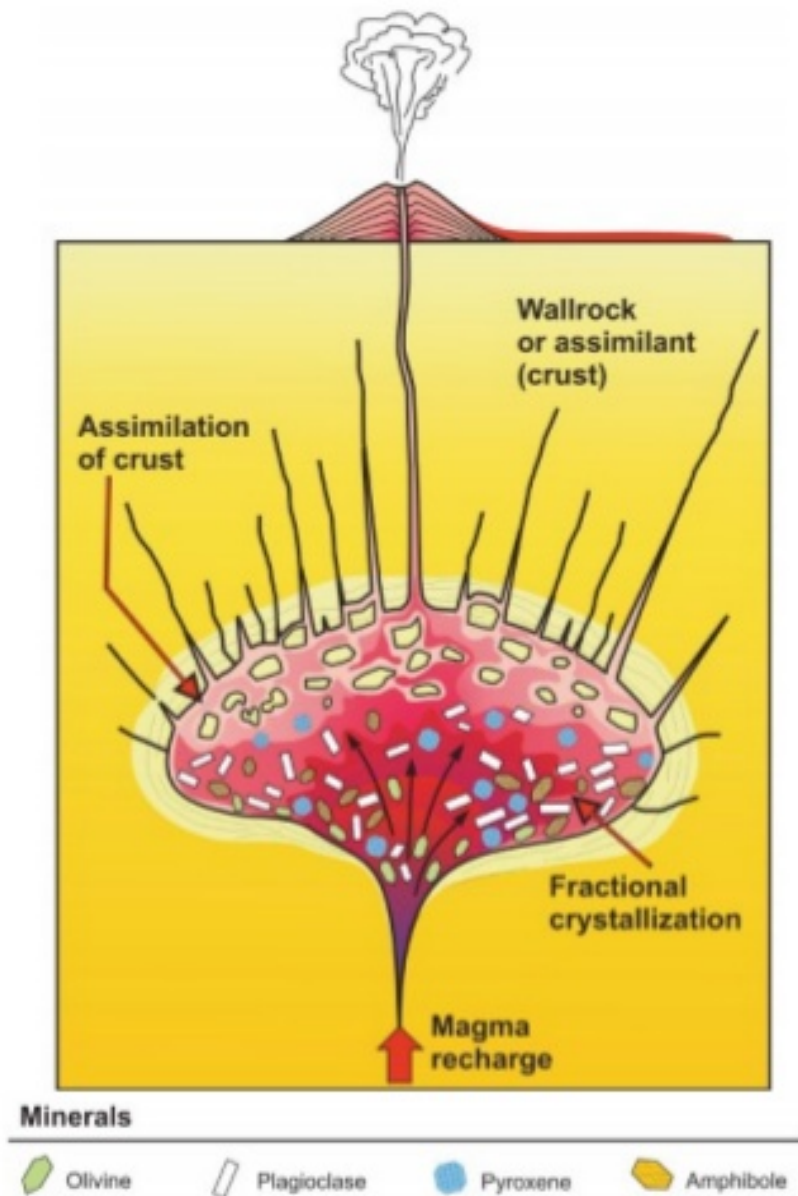# Modelling of Trace Element Behaviour in Igneous Systems

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Modelling of Trace Element Behaviour in Igneous Systems

Course Objectives

When you have completed this course you should be able to:

1. understand the principles behind petrogenetic modelling using trace elements;

2. predict how trace elements will behave during mantle melting and during passage of magma through the crust;

3. use EXCEL to carry out simple modelling of mantle melting and magma chamber processes

Syllabus

Session 1: Modelling Mantle Melting.

1 Partition Coefficients

2. Mantle Melting
   2.1 Definitions
   2.2 Batch Melting
   2.3 Fractional Melting
   2.4 Mantle Depletion
   2.5 Incremental Melting and Melting Columns

3. Practical: Modelling Mantle Melting using EXCEL

Session 2: Modelling Magma Chamber Processes

4. Mixing

5. Crystallization and Assimilation
   5.1 Fractional Crystallization
   5.2 Recharge and Fractional Crystallization (RFC)
   5.3 Assimilation + Fractional Crystallization (AFC)
   5.4 EC-RAFC

6. Practical: Modeling Magma Chamber Processes using EXCEL
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Note: The number of practical exercises covered will depend on the length of the course and the background of individual students. It will not be necessary to complete all exercises.

Section 1: Modelling Mantle Melting

1. Partition Coefficients

1.1 Partition Coefficients: Definitions

For trace element modelling, we need to understand the partitioning of trace elements between minerals and melt.

A **mineral/melt partition coefficient** for a given element is written $K_{i/l}$ where i is a mineral and l is a liquid (the melt).

More generally, we are interested in the **bulk distribution coefficient** for a given element, which is written as **D**. This is the sum of individual partition coefficients weighted according to their mass fractions, X_i.

$$D = \sum_{i=1}^{n} X_i\, K_{i/l}$$

If D>1, the element is **compatible**
If D<1, the element is **incompatible**

A simple **example** is shown below for the bulk distribution coefficient of Sr during crystallization of olivine (K_{ol}=0.01), clinopyroxene (K_{cpx}=0.2) and plagioclase (K_{pl}=2) in mass proportions 0.2:0.3:0.5.
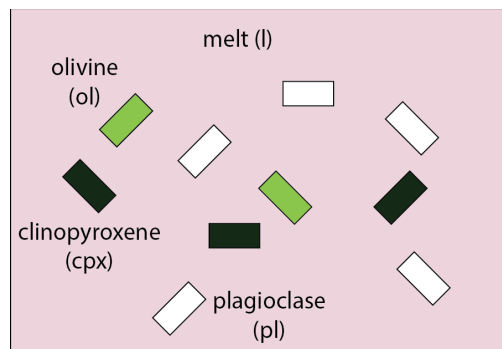
Wt. proportions	Sr partition coefficients
X_{ol}=0.2	K_{ol}=0.01
X_{cpx}=0.3	K_{cpx}=0.2
X_{pl}=0.5	K_{pl}=2.0

D_{Sr} = 0.2*0.01 + 0.3*0.2 +0.5*2 = 1.06

Therefore Sr is **slightly compatible**

1.2 Partition Coefficients: Dependencies

1.2.1 Variables

Partition coefficients may depend on:

Temperature (T)
Pressure (P)
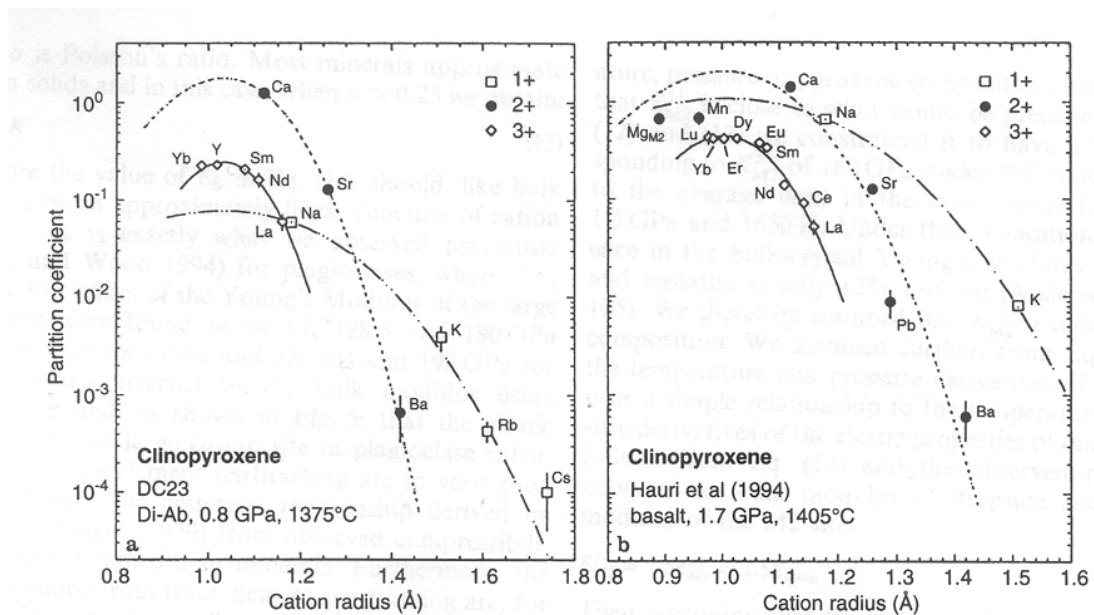**Melt composition (X_l)**
Mineral composition (X_M)
Oxygen fugacity (fO_2)

Thus **choosing partition coefficients appropriate for the system in question** is particularly important.

A key decision is **whether to keep partition coefficients constant** in a model or whether to allow them to vary as P, T etc. change.

1.2.2 Patterns of Trace Element Partitioning

Onuma et al. (1968) and Jensen (1973) wrote key papers on **patterns of trace element partitioning**.

 Log ($K_{i/l}$) v ionic rdius reveals a **parabolic relationship for each ionic charge**.

The peak of each parabola is the **optimum radius for a cation site in the mineral**.

1.2.3 Prediction of Partition Coefficients

Wood and Blundy (1997) found that **predicting the optimum site and the shape of the parabola** would enable **all the partition coefficients to be known.**
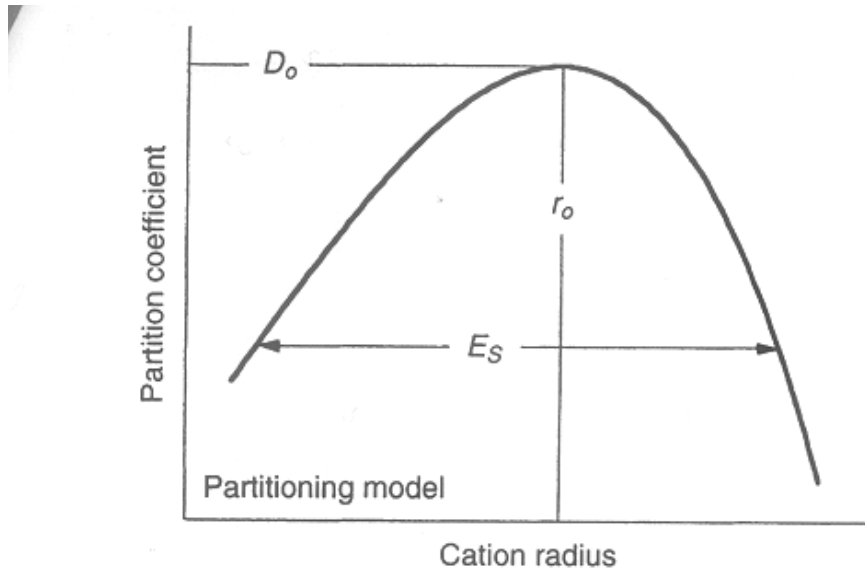
It is possible to use the **major element composition of the mineral to determine the optimum site radius**, and the **elasticity of the mineral structure to determine parabola shape**.

1.3 Choosing Partition Coefficients

Partition coefficients may be chosen by **one or more of**:

1. Finding values determined by **experiments or measurements** that **best match** the problem in hand.

2. Using, or making one's own, **compilations based on all reliable data** relevant to the problem at hand.

3. Using the Wood and Blundy (1997) method based on the **parabolic patterns of trace element partitioning** (can also use to extrapolate from incomplete partitioning data) .

4. Using **thermodynamic methods** such as those of Gaetani and Grove (1995) based on the calculation of partition coefficients expressed as equilibrium constants.

Essentially: the more effort put in to find optimum partition coefficients, the better the model. In this course, partition coefficients will be provided.

2. Mantle Melting

2.1 Definitions

To model mantle melting, we need to know (in addition to the partition coefficients) the relative contributions of the different minerals to the melt. These are termed the **reaction coefficients, p_i.**

The **bulk reaction coefficient** for a given element, written as **P**, is the sum of individual partition coefficients weighted according to the reaction coefficients.

$$P = \sum_{i=1}^{n} p_i K_{i/l}$$

Modelling then depends on the **type of melting** chosen:

Batch melting: the melt is in equilibrium with the mantle residue until in separates from it (segregates) and intrudes into the crust

Fractional melting: the melt separates from the mantle residue as soon as it is formed and contributes to a melt channel, which supplies melt to the crust

Critical melting: melting is fractional but the mantle has a porosity so that a small proportion is retained in pores before extraction.
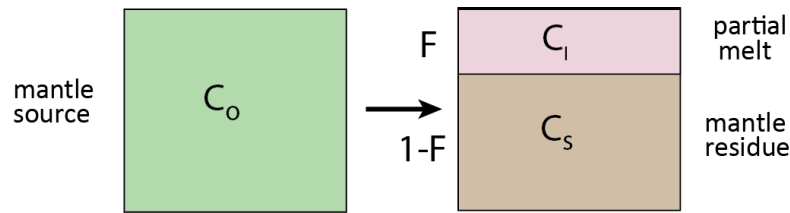
Incremental melting: increments of melt stay in equilibrium with the mantle residue before they separate and contribute to the melt channel.

and on **where the melting takes place**, when it might be:

isobaric (melting all at the same depth)

or **polybaric** (melting over a range of depths as in a melting column)

2.2 Batch Melting

F= mass fraction of melt; C = concentration of a given element in the mantle source (o), melt (l) and residual solid (s).

Mass balance requires that**: $C_o = FC_l + (1-F)C_s$**

By definition: **$C_s = DC_l$**

So we get the **batch melting equation:**

$$\frac{C_l}{C_0} = \frac{1}{F + D - FD}$$

For constructing a melting curve, the problem is that **D changes as melting progresses**. If the **phases enter the melt in a given proportion (p_i)**, this can be dealt with simply using the **initial bulk distribution coefficient, D_o** and the **bulk reaction coefficient P**:

$$D_o = \sum_{i=1}^{n} X_i^o K_{i/l}$$

$$P = \sum_{i=1}^{n} P_i K_{i/l}$$

which gives the **general batch melting equation**:

$$\frac{C_l}{C_0} = \frac{1}{F + D_o - FP}$$

For example, **spinel lherzolite mantle** containing **10 ppm Sr** is made up of **60% olivine, 25% orthopyroxene and 15% clinopyroxene** which melts in proportions **2: 1: 7**. Calculate the Sr content of the magma formed by **20% batch melting** given partition coefficients of 0.01 for ol/l, 0.05 for opx/l and 0.2 for cpx/l.

	X_i	p_i	$K_{i/l}$	$p_i K_{i/l}$	$X_i K_{i/l}$
olivine	0.6	0.2	0.01	0.002	0.006
orthopyroxne	0.25	0.1	0.05	0.005	0.0125
clinopyroxene	0.15	0.7	0.2	0.14	0.03
				P=0.147	**D_o=0.0485**

$$C_l = \frac{10}{0.2 + 0.0485 - 0.2 * 0.147} = 45.6 \ ppm$$

2.3 Fractional Melting

In pure fractional melting, the melt leaves the mantle as soon at it is formed. It then **accumulates to form pooled fractional melt**.
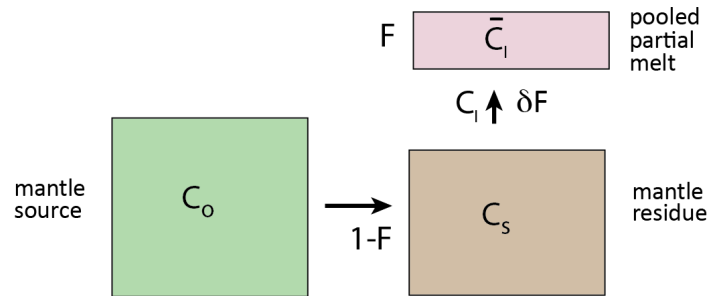
The **pooled (accumulated) melt composition, $\overline{C}_l$** is given by the expression (from Shaw, 1970):

$$\frac{\overline{C}_l}{C_o} = \frac{1}{F}\left[1 - \left(1 - \frac{PF}{D_o}\right)^{\frac{1}{P}}\right]$$

where, as before:

$$D_o = \sum_{i=1}^{n} X_i^o \, K_{i/l}$$

$$P = \sum_{i=1}^{n} P_i \, K_{i/l}$$

In **critical fractional melting**, the mantle has a porosity so that there is always trapped melt present. This may be modelled using the fractional melting equations but **calculating D by treating the trapped melt as a mineral with a D value of 1 and a reaction coefficient of 0**.
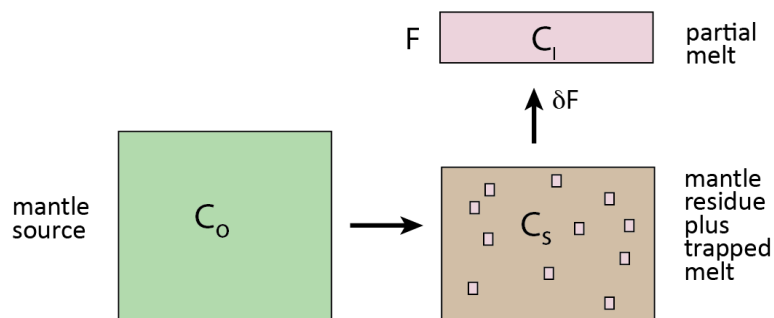
8

For example, **spinel lherzolite mantle** containing **10 ppm of Sr** is made up of **60% olivine, 25% orthopyroxene and 15% clinopyroxene** which melts in proportions **2: 1: 7**.

Calculate the Sr content of the magma formed by **20% fractional melting** given partition coefficients of 0.01 for ol/l, 0.05 for opx/l and 0.2 for cpx/l.

	X_i	p_i	$K_{i/l}$	$p_iK_{i/l}$	$XiK_{i/l}$
olivine	0.6	0.2	0.01	0.002	0.006
orthopyroxene	0.25	0.1	0.05	0.005	0.0125
clinopyroxene	0.15	0.7	0.2	0.14	0.03
				P=0.147	**D_o=0.0485**

$$\frac{\overline{C_l}}{C_o} = \frac{1}{F}\left[1 - \left(1 - \frac{PF}{D_o}\right)^{\frac{1}{P}}\right] = 49.9 \, ppm \, (F = 0.2)$$

Pooled fractional melting thus gives higher melt concentrations of **incompatible elements than batch melting.** This is because the melt released has no opportunity to r-equilibrate with the mantle.

Critical fractional melting may be calculated by inserting a row for a new phase melt with a melting rate (p) of 0 and a partition coefficient (K) of 1. **Its proportion is the porosity expressed as a mass fraction**, here 0.02. A new column (X_i') is also needed to multiply the mineral proportions by (1-porosity) so that the phases still sum to 100%:

	X_i	X'_i	p_i	$K_{i/l}$	$P=p_iK_{i/l}$	$Do=XiK_{i/l}$
olivine	0.60	0.588	0.2	0.01	0.002	0.00588
orthopyroxene	0.25	0.245	0.1	0.05	0.005	0.01225
clinopyroxene	0.15	0.147	0.7	0.20	0.14	0.0294
melt		0.02	0	1.00	0	0.02
					P=0.147	**D_o =0.067**

The same calculation is then carried out for the **new value of D_o**.

$$\frac{\overline{C_l}}{C_o} = \frac{1}{F}\left[1 - \left(1 - \frac{PF}{D_o}\right)^{\frac{1}{P}}\right] = 49.0 \, ppm \, (F = 0.2)$$

Because this **new value of D_o is higher than in pure fractional melting**, the **concentrations of incompatible elements in the melt are lower**.

Note that **setting the melt fraction to 0** in the critical melting grid above is the **same as having pure fractional melting,** Thus the grid can be used for both types of melting.

2.4 Melting Trends

Rather than calculating single values, it is useful to **calculate melting trends**. These can show how **elements or element ratios vary with degree of melting** (F), or they can be **trends on element-element or element ratio plots**.

To calculate melting trends, it is necessary to first **make a Table with a column for F and a column for the calculated value of c_l.** For the simpler batch melting equation, the equation can be written as a single expression..

$$\frac{C_l}{C_0} = \frac{1}{F + D_o - FP}$$

| F	$C_l(Sr)$
0.01	175.35
0.02	152.53
0.03	134.97
0.04	121.04
0.05	109.71
0.06	100.32
etc	etc.
0.20	45.64

For the more complex fractional melting equation it may be a good idea to **break the equation into its parts** so that errors are easier to find and correct – as shown in the columns below.

The fractional (critical) melting calculation is given below using the equation, and values of P and D_o and porosity from the previous page. The mantle Sr concentration is 10ppm as before.

$$\frac{\overline{C_l}}{C_o} = \frac{1}{F}\left[1 - \left(1 - \frac{PF}{D_o}\right)^{\frac{1}{P}}\right]$$

F	1/F	1/P	PF/Do	C_{Sr}
0.01	100.00	6.80	0.02	**139.05**
0.02	50.00	6.80	0.04	**130.63**
0.03	33.33	6.80	0.07	**122.78**
0.04	25.00	6.80	0.09	**115.48**
0.05	20.00	6.80	0.11	**108.67**
0.06	16.67	6.80	0.13	**102.35**
etc.				**etc.**
0.20	5.00	6.80	0.44	**48.98**

The **trends for Sr against F** for batch melting, pure fractional pooled melting and critical fractional pooled melting (2% porosity) are shown on the **next page**.
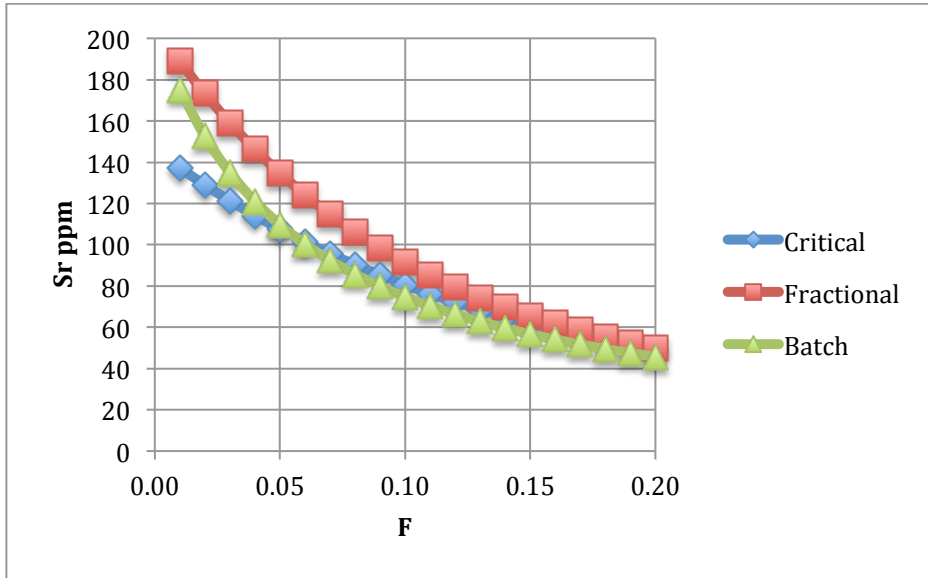
Note that **differences in the type of melting are greatest in this case for low degrees of melting**. At higher degrees of melting, differences are small.

There are many examples of application of melting trends. In the one below, **modelling of element ratios is used to determine the depth and degree of melting of some magmas form western Turkey**. They show a low degree of melting (<10%) of deep mantle (garnet lherzolite) that has an enriched composition (WAM = Western Anatolia Mantle).
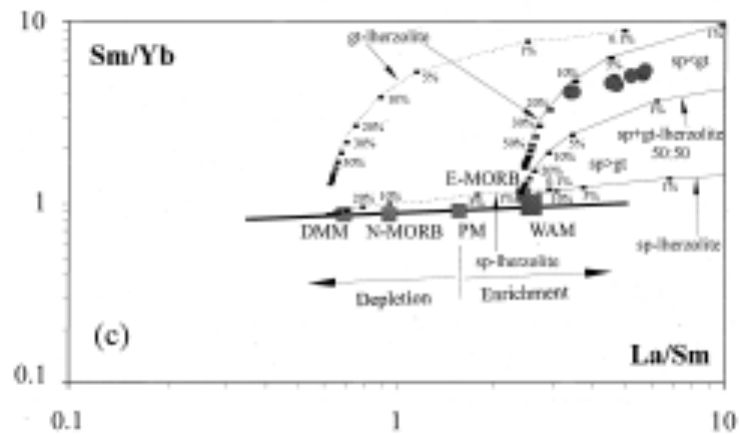
2.5 Modelling the Mantle

Just as equations can be written to calculate trace element concentrations in the magma produced by partial melting, so **equations can be written to calculate the concentrations of trace elements in the mantle residues**. As would be expected, there are **different equations for batch and fractional melting**.

As before:

C_o = concentration of a trace element in the original mantle
C_s = concentration of a trace element in the solid mantle residue
C_l = concentration of a trace element in the melt
F = degree of partial melting
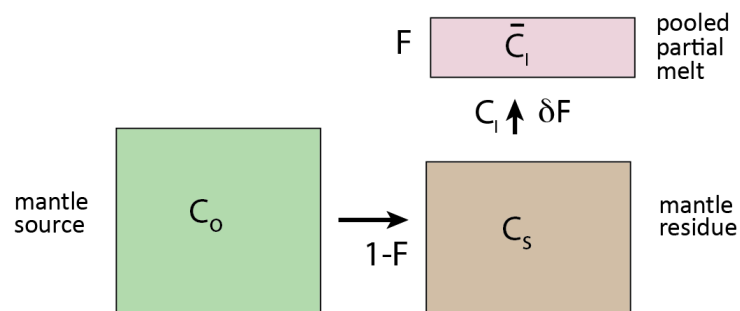D_o = initial bulk distribution coefficient
P = bulk reaction coefficient

Depletion by Batch Melting
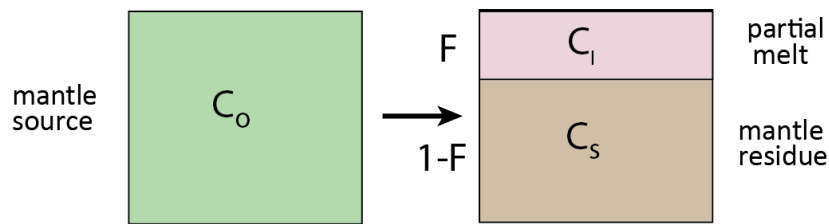
$$\frac{C_s}{C_0} = \left[\frac{D_o - PF}{1 - F}\right]\left[\frac{1}{D_o + F(1 - P)}\right]$$

Depletion by Pooled Fractional Melting

$$\frac{C_s}{C_o} = \frac{1}{1 - F}\left[\left(1 - \frac{PF}{D_o}\right)^{\frac{1}{P}}\right]$$

2.5.1 Mantle Depletion Calculations

	X_i	p_i	$K_{i/l}$	$p_iK_{i/l}$	$X_iK_{i/l}$
olivine	0.6	0.2	0.01	0.002	0.006
orthopyroxene	0.25	0.1	0.05	0.005	0.0125
clinopyroxene	0.15	0.7	0.2	0.14	0.03
				P=0.147	**D_o=0.0485**

Batch Melting (Sr_0=10ppm, F=0.2,)

$$\frac{C_s}{C_0} = \left[\frac{D_o - PF}{1 - F}\right]\left[\frac{1}{D_o + F(1 - P)}\right]$$

Batch melting: C_s=1.09 ppm

Pure fractional melting (Sr_0 =10ppm, F=0.2)

$$\frac{C_s}{C_o} = \frac{1}{1 - F}\left[\left(1 - \frac{PF}{D_o}\right)^{\frac{1}{P}}\right]$$

Pure fractional melting: C_s=0.02 ppm

Critical fractional melting (Sr_0 =10ppm, F=0.2, porosity = 2%)

|	X_i	X_i	p_i	$K_{i/l}$	$P=p_iK_{i/l}$	$D_o=X_iK_{i/l}$
olivine	0.60	0.588	0.2	0.01	0.002	0.00588
orthopyroxene	0.25	0.245	0.1	0.05	0.005	0.01225
clinopyroxene	0.15	0.147	0.7	0.20	0.14	0.0294
melt		0.02	0	1.00	0	0.02
					0.147	**0.06753**

Critical melting: C_s=0.27 ppm

Pure fractional melting gives the **greater depletion of incompatible elements in the mantle residue. Batch melting** gives the **least.**

Note: the **type of melting is much more important for peridotites** than for basalts.

2.5.2 Mantle Depletion Trends

As with melts, it is possible to construct trends to show how mantle compositions change with increasing degree of partial melting.
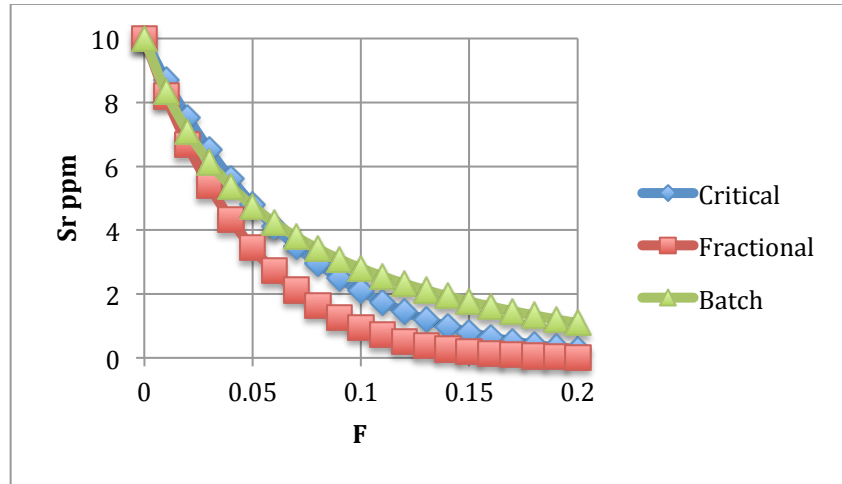
There are many published examples of how mantle modelling can improve our understanding of exposures of mantle rocks. The plot below applies modelling to the interpretation of mantle rocks from the Troodos Massif. It was modelled using the **batch melting equation (green line)** and **fractional melting equation (brown line**) in spinel and garnet (red line) facies.

The modelling **distinguishes between spinel and garnet faces** (i.e. depth of melting) and **type of melting** (batch or fractional). It shows that c. 20-25% of critical fractional melting best explains the compositions.
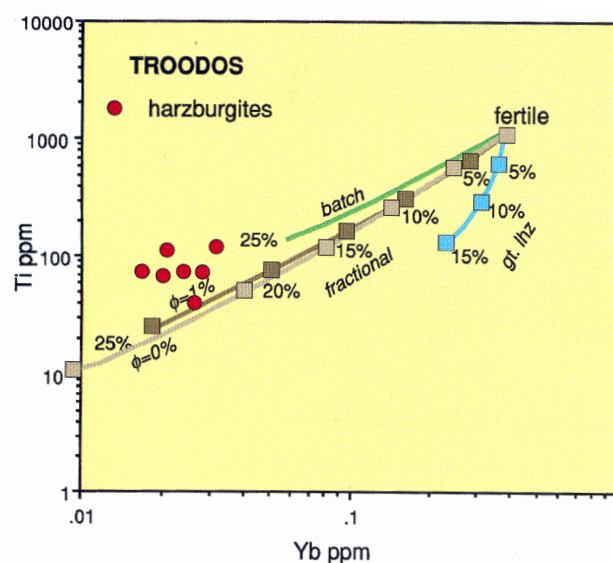
2.6 Incremental Melting and Melting Columns
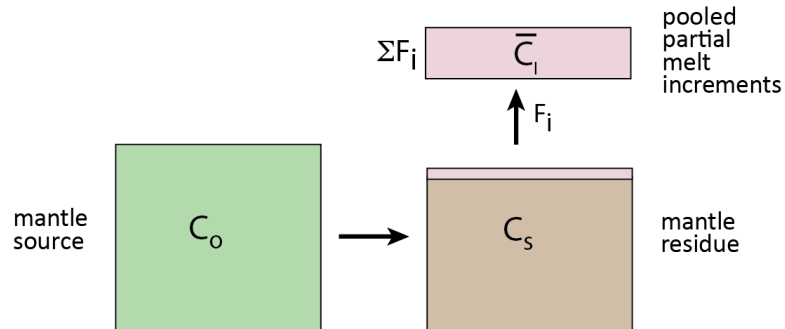
Incremental melting is somewhere between batch melting and critical fractional melting: small batches of magma equilibrate with the mantle before extraction. It may be modelled **using the batch melting equation for each increment**, recalculating mantle composition and mineralogy between increments. **The composition is recalculated** using the batch melting equation in Section 2.4.1, i.e.

$$\frac{C_s}{C_0} = \left[\frac{D_o - PF}{1 - F}\right]\left[\frac{1}{D_o + F(1 - P)}\right]$$

The **mineralogy is recalculated** using the expression:

$$X_i' = \frac{X_i^o - F_{inc}p_i}{1 - F_{inc}}$$

where $X_i°$ are the composition before the melting increment
X_i' are the new mass fractions following extraction of the melt increment
F_{inc} is the degree of melting for the met increment
p_i are the reaction coefficients

2.6.1 Incremental Melting: Calculation Method

Spinel lherzolite mantle containing **10 ppm of Sr** is made up of **60% olivine, 25% orthopyroxene and 15% clinopyroxene** which melts in proportions **2: 1: 7**.

It melts in two stages. The first by 10% batch melting, the second by a further 10% batch melting.

Calculate the Sr content of the magma formed by **20% incremental (2 x 10%) melting** given partition coefficients of 0.01 for ol/l, 0.05 for opx/l and 0.2 for cpx/l.

	X_i	p_i	$K_{i/l}$	$p_iK_{i/l}$	$X_iK_{i/l}$
olivine	0.6	0.2	0.01	0.002	0.006
orthopyroxne	0.25	0.1	0.05	0.005	0.0125
clinopyroxene	0.15	0.7	0.2	0.14	0.03
				P=0.147	**D_o=0.0485**

$$C_l = \frac{10}{0.1 + 0.0485 - 0.1 * 0.147} = 74.4\ ppm$$

Calculate the new mineral proportions (X_i') at F=0.1:

	X_i	p_i	X_i'
olivine	0.6	0.2	0.644
orthopyroxne	0.25	0.1	0.267
clinopyroxene	0.15	0.7	0.089

Calculate the new mantle composition at F=0.1:

$$\frac{C_s}{C_o} = \frac{1}{1-F}\left[\left(1 - \frac{PF}{D_o}\right)^{\frac{1}{P}}\right] = 2.81\ ppm$$

Repeat the calculation using the batch melting equation:

|	X_i	p_i	$K_{i/l}$	$p_iK_{i/l}$	$X_iK_{i/l}$
olivine	0.644	0.2	0.01	0.002	0.0064
orthopyroxne	0.267	0.1	0.05	0.005	0.013
clinopyroxene	0.089	0.7	0.20	0.14	0.0178
				0.147	**0.0376**

$$C_l = \frac{2.81}{0.1 + 0.0376 - 0.1 * 0.147} = 22.9\ ppm$$

The pooled melt by mass balance is then:

$$C_l = \frac{0.1 * 74.4 + 0.1 * 22.9}{0.1 + 0.1} = 48.6\ ppm$$

2.6.2. Melting Columns

Most models assume that **incremental melt fractions are extracted into a channel** after which they no longer react with the residual phases,

GPa	D_o	P
1.5	0.13	0.42
2.5	0.10	0.34
3.5	0.47	1.29
4.5	0.39	0.77
5.5	0.31	0.54
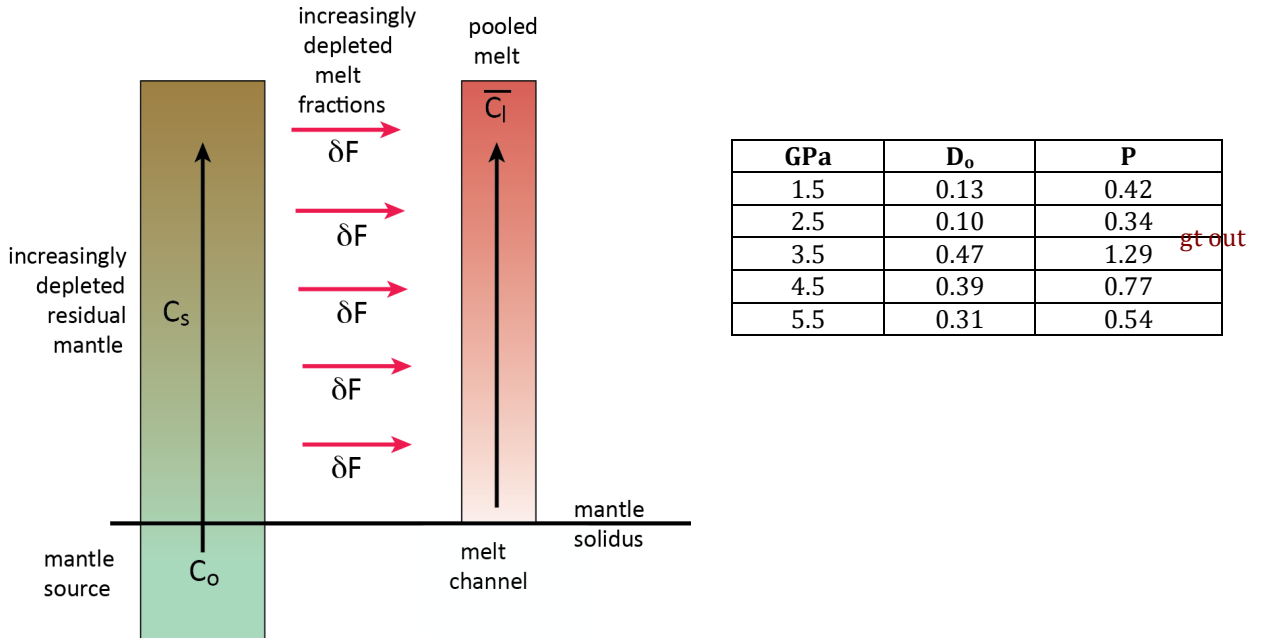
To model melting columns, it is easiest to carry out the calculation method in Section 2.6.1 but for **small batch melting increments (e.g. F_{inc}=0.02), each with recalculated values of C_s, and X_o.** In a melting column, recalculation must be **based not only on the loss of melt, but also on the effects of changing pressure on mantle mineralogy.** This is not difficult, but it is time-consuming, and so beyond the scope of this course.

3. Practical: Modelling Mantle Melting Using EXCEL

3.1 Batch Melting Exercise

Task 1. This first task is to reproduce the Tables and plots in Section 2 that relate to batch melting. Start by **opening an EXCEL Spreadsheet**. Label it and remember to save it periodically!

Now rename the first Worksheet (Sheet1) as **'Batch Melting'**.

Task 2. Start by entering the known data into part of the grid:

	X_i	p_i	$K_{i/l}$	$p_iK_{i/l}$	$XiK_{i/l}$
olivine	0.6	0.2	0.01		
orthopyroxene	0.25	0.1	0.05		
clinopyroxene	0.15	0.7	0.20		
				P=	**D$_o$=**

Calculate the final two columns using the equations from Section 2.2. Then sum them and put the sum into the grid squares marked P= and D$_o$=. Check that your calculations are correct by comparison with the grid in Section 2.2.

Task 3. Now **set up a partial melting grid** with the first column having increasing degree of melting (F) from 0.01 (1%) to 0.2 (20%) and the second column calculating the Sr concentration (see below) for degrees of melting from 1 to 20% using the batch melting equation:

$$\frac{C_l}{C_0} = \frac{1}{F + D_o - FP}$$

F	C_l(Sr)
0.01	
0.02	
0.03	
0.04	
0.05	
0.06	
etc	etc.
0.20	

[note that recalculations are needed if one of the mantle minerals melts out; this does not apply here]

Task 4. Make a **plot of Sr concentration against degree of melting (F)** as in Section 2.4 and check that it matches the batch melting graph in that Section.

3.2 Fractional Melting Exercise

Task 1. The aim is to repeat the exercise but now for fractional melting (where melt is separated from the mantle as soon as it forms)

Start by creating a **new worksheet** (click on '+') and label it **'Fr. Melting'**.

Task 2. Copy and paste the data box from the "Batch Melting" worksheet onto the "Fr. Melting" worksheet. Use the fractional melting equation (reproduced below) to produce the equivalent grid with columns for F and C_l.

$$\frac{\overline{C_l}}{C_o} = \frac{1}{F}\left[1 - \left(1 - \frac{PF}{D_o}\right)^{\frac{1}{P}}\right]$$

The difference between this and batch melting is the greater complexity of the equations. As explained in the Section 2.4, my recommendation is **break the equation into parts** as that makes it easier to identify any errors.

The Table in Section 2.4 (see below, without the results of the calculations) shows the equation can be split into a number of columns. Repeat this (or write a single equation if you wish) to reproduce the Table and check it for errors.

F	1/F	1/P	PF/D_o	C_{Sr}
0.01				
0.02				
0.03				
0.04				
0.05				
0.06				
etc.				
0.20				

Task 3. **Plot the fractional melting trend for Sr** and check it against the graph in Section 2.4.

3.3 Critical Melting Exercise

Task 1, As critical melting is simply a form of fractional crystallization, you can continue to work with the **"Fr. Xn" worksheet**.

Task 2. Copy the fractional melting data box onto the adjacent space on the spreadsheet. **Insert a column and row into the worksheet** as in Section 2.3 and reproduced in part below. The added row is for the trapped melt, and the column for the recalculated proportions of phases. Take enter the mass proportion of 0.02 for melt in the X' column and **complete the Table**. Check that it is correct by comparing it with the Table in Section 2.3.

	X_i	X'_i	p_i	$K_{i/l}$	$P=p_iK_{i/l}$	$D_o=X_iK_{i/l}$
olivine	0.60		0.2	0.01		
orthopyroxene	0.25		0.1	0.05		
clinopyroxene	0.15		0.7	0.20		
melt	0					
					P=	**D =**

Task 3. Now use your values for P and D_o to **complete the Table for the C_l-F plot** (below). Check against the Table in Section 2.4 to ensure that it is correct.

F	1/F	1/P	PF/Do	C_l(Sr)
0.01				
0.02				
0.03				
0.04				
0.05				
0.06				
0.07				
0.08				
0.09				
0.10				
0.11				
0.12				
0.13				
0.14				
0.15				
0.16				
0.17				
0.18				
0.19				
0.20				

Task 4. Plot the graph of C_l v F for the critical melting and check against the plot in Section 2.4 to ensure that it is correct.

3.3 Modelling Mantle Depletion

Task 1. Name a **new worksheet 'Mantle'**. Your aim is to repeat the Exercises in Section 2.5.

Start by copying the "Batch Melting" data box into the 'Depletion' spreadsheet.

Task 2. **Calculate the Sr concentration in the mantle** (originally 10 ppm) during batch melting using the batch melting depletion equation (reproduced below):

$$\frac{C_s}{C_0} = \left[\frac{D_o - PF}{1 - F}\right]\left[\frac{1}{D_o + F(1 - P)}\right]$$

Do this by setting up and completing the grid below using D_o, P and F from the data box you pasted into the worksheet. Don't forget to multiply by C_o in calculating the final column.

F	D_o-PF	1-F	D_o-F(1-P)	C_l(Sr)
0				
0.01				
0.02				
0.03				
Etc.				
0.20				

Task 3. **Plot a graph of Sr in the mantle v degree of batch melting**. Check it against the graph in Section 2.5.2.

Task 4. Now insert the data box for critical melting from the 'Fr. Xn" worksheet. Using what you have learnt so far, and using the equation below, attempt to **plot similar trends to those in Task 3 but for pure fractional melting and critical melting** with a porosity of 0.02. Check your plots against the graphs in Section 2.5.2.

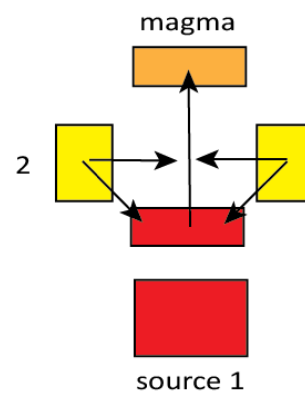$$\frac{C_s}{C_o} = \frac{1}{1 - F}\left[\left(1 - \frac{PF}{D_o}\right)^{\frac{1}{P}}\right]$$

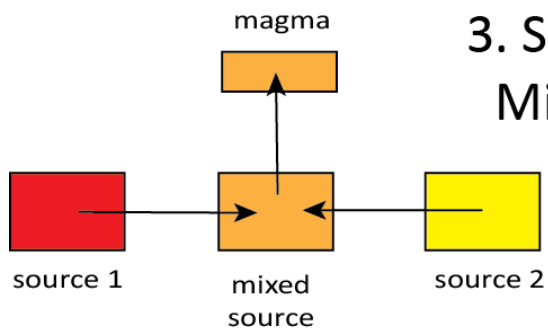# Session 2: Modelling Magma Chamber Processes

4. Mixing

Mixing is important in magma genesis. As shown below, it can take place **in the mantle** (mixing of magma sources such as a subduction component and a mantle wedge) or **in the magma chamber** (mixing of magma with crust, or mixing of two magmas). Here we will model **mixing of magmas in a magma chamber**.
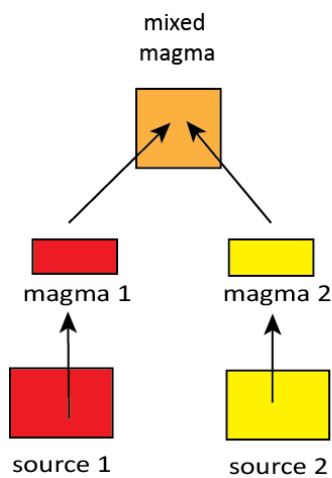
4.1 Magma Chamber Mixing

The simplest way to calculate the composition of mixed magmas is using the **mass balance equation**. Consider the mixing of a basalt and rhyolite magma.

$$C_{mix} = X_{rhy}C_{rhy} + (1 - X_{rhy})C_{bas}$$

where: **C_{bas}, C_{rhy} and C_{mix}** are the concentrations of an element in basalt, rhyolite and the mixture; and **X_{rhy}** is the mass fractions of the rhyolite in the basalt-rhyolite mixture.

For example: La in basalt = 15 ppm and in rhyolite =100ppm. Then in a 40:60 mixture, La_{mix}= 0.6. 100 + 0.4. 15 = 66 ppm

In EXCEL, it is a straightforward task to construct a grid of the type below. The end member compositions are put in at top and bottom and the **mass balance equation used to calculate the intermediate values**.

	X_{rhy}	La	Sm	Tb	Yb	La/Sm	Tb/Yb
basalt	0.0	15.0	10	10	10	1.50	1.0
	0.1	23.5	14	11	10	1.68	1.1
	0.2	32.0	18	12	10	1.78	1.2
	0.3	40.5	22	13	10	1.84	1.3
	0.4	49.0	26	14	10	1.88	1.4
	0.5	57.5	30	15	10	1.92	1.5
	0.6	66.0	34	16	10	1.94	1.6
	0.7	74.5	38	17	10	1.96	1.7
	0.8	83.0	42	18	10	1.98	1.8
	0.9	91.5	46	19	10	1.99	1.9
rhyolite	1.0	100.0	50	20	10	2.00	2.0

The grid can then be used to plot a mixing line, such as that below:
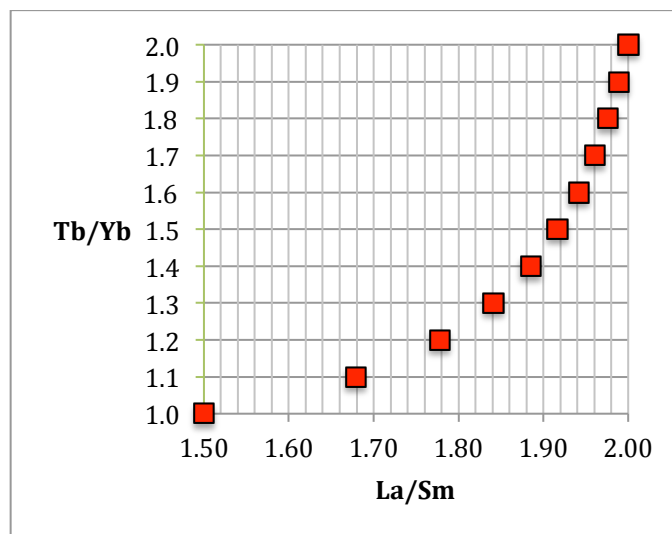
4.2 Magma Mixing Equation

The general two-component mixing equation is a hyperbola:

$$Ax + Bxy + Cy + D = 0$$

Where x and y are two variables (elements or element ratios), and A, B, C, and D are coefficients of the variables.

For plotting, this **equation can be re-arranged** to give y as a function of x:

$$y = -\frac{Ax + D}{Bx + c}$$

Original sources: Vollmer (1976); Langmuir et al. (1977).

The **solution to this equation** is well-known and shown below. It looks complicated but is actually very straightforward, as will be seen

$A = a_2 b_1 y_2 - a_1 b_2 y_1$
$B = a_1 b_2 - a_2 b_1$
$C = a_2 b_1 x_1 - a_1 b_2 x_2$
$D = a_1 b_2 x_2 y_1 - a_2 b_1 x_1 y_2$

where

a_1 = denominator of y in end member 1
b_1 = denominator of x in end-member 1
a_2 = denominator of y in end-member 2
b_2 = denominator of x in end-member 2
x_1 = ratio x in end-member 1
y_1 = ratio y in end-member 1
x_2 = ratio x in end-member 2
x_2 = ratio y in end-member 2

Taking the same e**xample** as before, but with different ratios:

Basalt: La=15ppm; Sm=10ppm; Tb=10ppm; Yb=10ppm
Rhyolite: La=100ppm; Sm=50ppm; Tb=20ppm; Yb=10ppm

<center>La/Yb (x) v Tb/Yb (y)</center>

a_1 = denominator of y in end member 1.... **Yb=10**

b_1 = denominator of x in end-member 1.... **Yb=10**

a_2 = denominator of y in end-member 2..... **Yb=10**

b_2 = denominator of x in end-member 2.... **Yb=10**

x_1 = ratio x in end-member 1..... .**La/Yb=1.5**

y_1 = ratio y in end-member 1...... **Tb/Yb =1.0**

x_2 = ratio x in end-member 2...... **La/Yb=10.0**

y_2 = ratio y in end-member 2...... **Tb/Yb=2.0**

$A = a_2 b_1 y_2 - a_1 b_2 y_1$ = **100**
$B = a_1 b_2 - a_2 b_1$ = **0**
$C = a_2 b_1 x_1 - a_1 b_2 x_2$ = **-850**
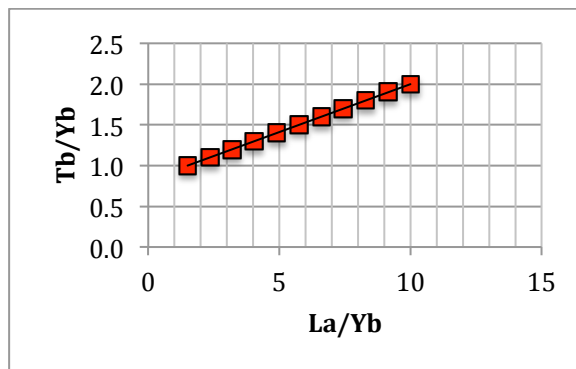$D = a_1 b_2 x_2 y_1 - a_2 b_1 x_1 y_2$ = **-100**

$$y = -\frac{Ax + D}{Bx + c}$$

as B=0

$$y = -\frac{A}{C}x - \frac{D}{C}$$

substituting A, C and D, gives the equation:

$$\frac{Tb}{Yb} = 0.12\frac{La}{Yb} - 0.12$$

The concept of straight line mixing for ratios with common denominators is **important in choosing trace element and isotope projections**

<center>25</center>

5. Crystallization and Assimilation

Like melting, magma chamber modeling can be simple, but it then becomes progressively complicated as attempts to reproduce reality increase.

Once thought to be closed systems that simply crystallized as they cooled, they are now known mostly to be **open systems** which involve **not just crystallization but also recharge, assimilation and eruption**, as well as crystallization complexities such **magma-crystal reaction, filter-pressing, volatile transfer and diffusion**.
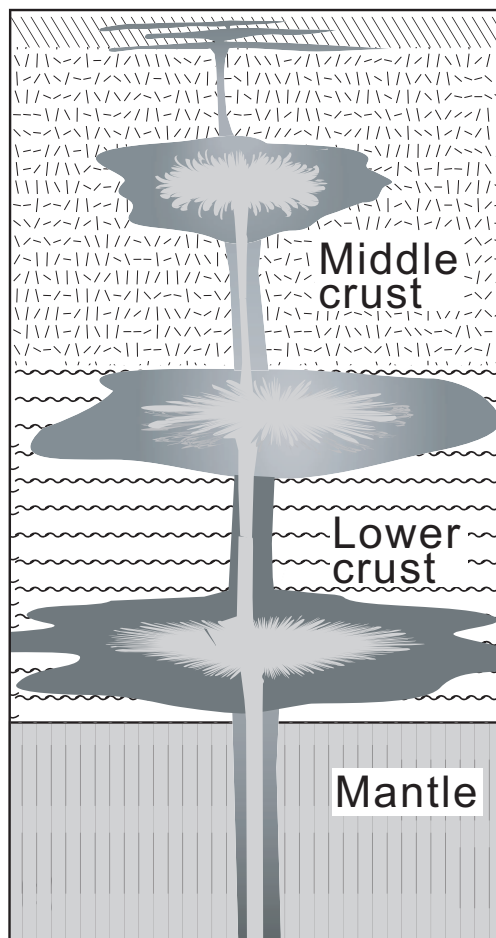
5.1 Fractional Crystallization
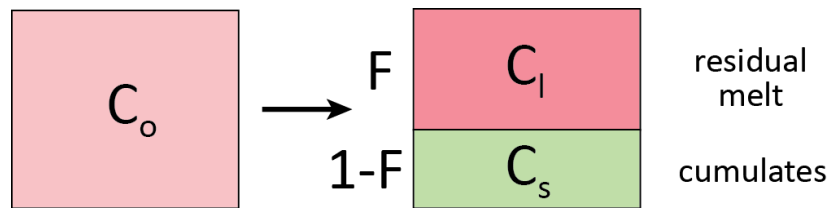
Fractional crystallization is the same concept as fractional melting in that crystals are extracted as soon as they form without re-equilibrating with the melt. It is usually **modeled using the Rayleigh Fractionation Equation**:

$$\frac{C_l}{C_o} = F^{D-1}$$

As before: **D**= bulk distribution coefficient
F= the mass fraction of melt remaining
C$_o$ is the concentration of an element in the initial magma
C$_l$ is the concentration in the final magma
C$_s$ (in the Figure only) is the concentration in the residual solid.

One feature of this equation is that relationships are typically **linear in logarithmic space**.

For example, taking logs of the Rayleigh equation itself:

$$Log(C_l) = (D-1)Log(F) + Log(C_o)$$

This means that a logarithmic plot of **C$_l$ against F will be linear with a slope of (D-1)**

5.1.1 Element-Element plots

Element-element and element ratio plots are similarly linear in logarithmic space. To see why, **start with the Rayleigh equation**:

$$\frac{C_l}{C_o} = F^{(D-1)}$$

Take logs for elements A and B

$$Log(C_l^A) - Log(C_o^A) = (D^A - 1)Log(F)$$

$$Log(C_l^B) - Log(C_o^B) = (D^B - 1)Log(F)$$

Substitute for Log(F) to give a straight-line equation, i.e. of form y=mx+c:

$$Log(C_l^A) = \frac{D^A - 1}{D^B - 1}Log(C_l^B) + c$$

Thus if we plot two elements in logarithmic space, we get a **straight line with a slope of $(D^A\text{-}1)/(D^B\text{-}1)$**
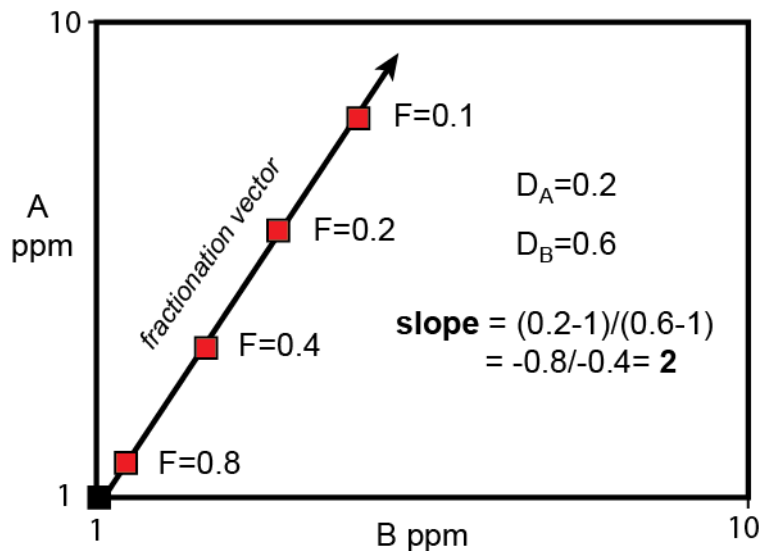
We can therefore **draw vectors for individual minerals and mineral assemblages** and compare these with observed variations (Pearce & Norry, 1979).

Example: A basic magma containing 100 ppm Sr and 50 ppm Zr crystallizes a mixture of 20% olivine, 30% clinopyroxene and 50% plagioclase. **Plot a graph of Sr v Zr showing vectors** for the individual minerals and bulk crystallizing assemblage. Partition coefficients for basic magmas are, for Sr: $K_{ol/l}=0.01$; $K_{cpx/l}=0.2$ & $K_{pl/l}=2$. For Zr: $K_{ol/l}=0.01$; $K_{cpx/l}=0.15$ & $K_{pl/l}=0.02$.

To plot vectors using EXCEL, it is necessary to set up a grid of the sort shown below for Sr. The top three rows enable the individual mineral vectors to be drawn. The bottom row is used for the bulk assemblage vector. **The Rayleigh equation is used to calculate C_l for different values of F**. Note that **F here refers to melt remaining**, so F=1 is no crystallization and F=0.5 is 50% of melt remaining.

	X_i	K_i (Sr)	C_o(F=1)	C_l (F=0.75)	C_l (F=0.5)
olivine	0.2	0.01	300	398.85	595.86
clinopyroxene	0.3	0.2	300	377.64	522.33
plagioclase	0.5	2	300	225.00	150.00
		D(Sr)			
ol.2+cpx.3+pl.5		1.062	300	294.70	287.38

Repeating this grid for Zr allows the plot below to be drawn.
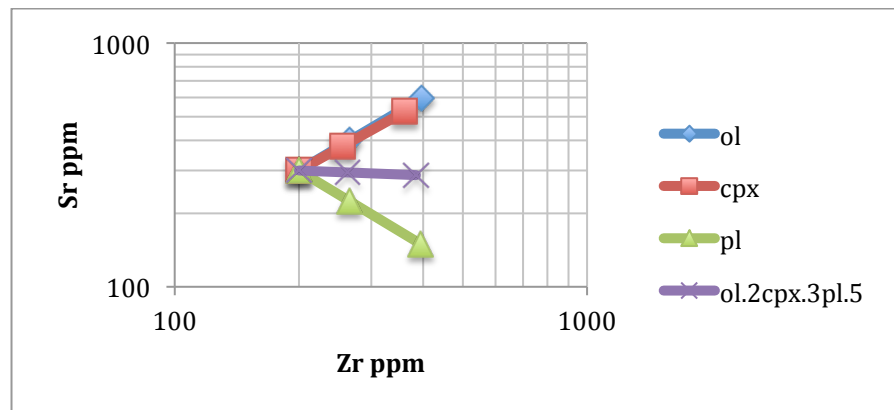
The Figure below shows a **real example** of how the fractionation vectors can help to interpret a volcanic sequence (From Pearce et al., 1990). **Three distinctive fractionation trends** can be identified, each requiring a different mineral assemblage.
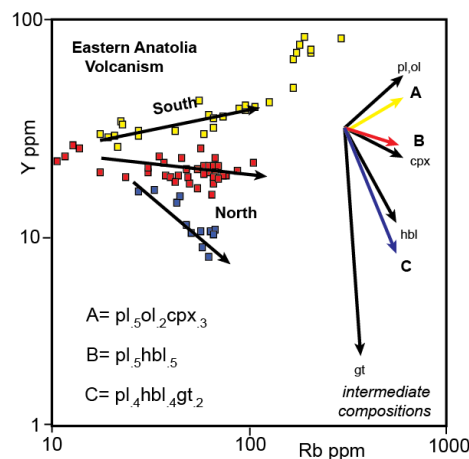
5.3 Recharge and Fractional Crystallization (RFC)

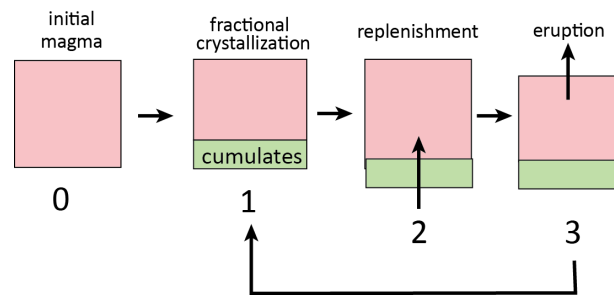The concept and **modeling of open-system magma chambers** principally originates from O'Hara (1977) and O'Hara and Mathews (1981).

They considered **replenishment (recharge by magma addition) and assimilation of the magma chamber roof** and demonstrated that trace elements in the magma can reach steady stage compositions if parameters are constant.

Although they quantified the process with some long equations, it is arguably much easier to model now using spreadsheets – as shown here.

5.3.1 The FRE Cycle

To carry out the modeling, we need to define the FRE cycle where:

F= the mass fraction of melt left in each crystallization cycle
I= the mass fraction of new melt added during the replenishment
E=the mass fraction of melt lost during the eruption

If F, I and E are all reported as mass fractions of the initial magma, then the **magma chamber will have constant mass if F+I-E=1.** If so, the equations are:
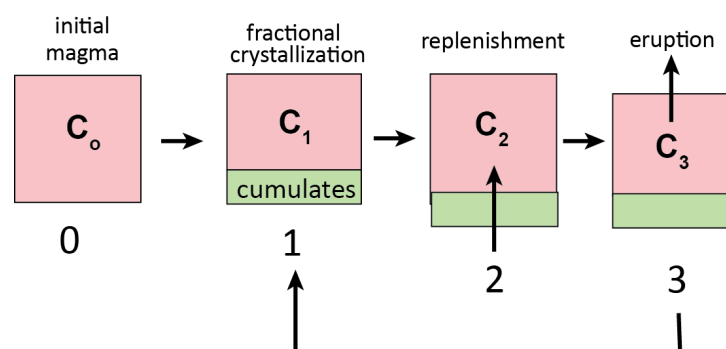
$$C_o \text{ to } C_1 \text{ } (first \text{ } fr. Xn \text{ } event): \text{ } C_1 = C_o F^{D-1}$$

$$C_1 \text{ to } C_2 \text{ } (recharge): \text{ } C_2 = \frac{FC_1 + IC_o}{F + I}$$

$$C_2 \text{ to } C_3 \text{ } (eruption): \text{ } C_3 = C_2$$

$$C_3 \text{ to next cycle } C_1 \text{ } (subsequent \text{ } fr. Xn \text{ } events). \text{ } C'_1 = C_3 F^{D-1}$$

5.3.2 Recharge-Fractional Crystallization (RFC) Modelling

To **model RFC using EXCEL**, first set up a data box with values for C_o, D, F, I and E. Make sure F+I-E=1, otherwise the maths is more complicated.

Then set up the grid, as shown for Zr (C_o=100ppm; D=0.04) below,

	cycle 1=C_o then = C_3	C_1	C_2	C_3
cycle	Comp.	Fr Xn	Replen.	Eruption
1	100.00	110.64	109.12	109.12
2	109.12	120.74	117.78	117.78
3	117.78	130.31	125.98	125.98
4	125.98	139.39	133.76	133.76
5	133.76	148.00	141.14	141.14
6	141.14	156.17	148.14	148.14
7	148.14	163.91	154.78	154.78
8	154.78	171.26	161.08	161.08
9	161.08	178.22	167.05	167.05
10	167.05	184.83	172.71	172.71

Co	100.00
D	0.04
F	0.90
I	0.15
E	0.05

If F, I and E are constant, and the grid is extended to large numbers of cycles. Here, the magma composition reaches a **steady state at 277 ppm after 127 cycles and 276.71 at 173 cycles.**

126	276.49	305.92	276.50	276.50
127	276.50	305.93	276.51	276.51
128	276.51	305.95	276.52	276.52

172	276.70	306.16	276.71	276.71
173	276.71	306.16	276.71	276.71
174	276.71	306.16	276.71	276.71

The plot below shows the change in Zr concentration with increasing number of FRE cycles. The result can be **incompatible element enrichment while the magma composition stays basaltic.** Varying F, I and E will, of course, change the shape of the curve and the steady state value.

31
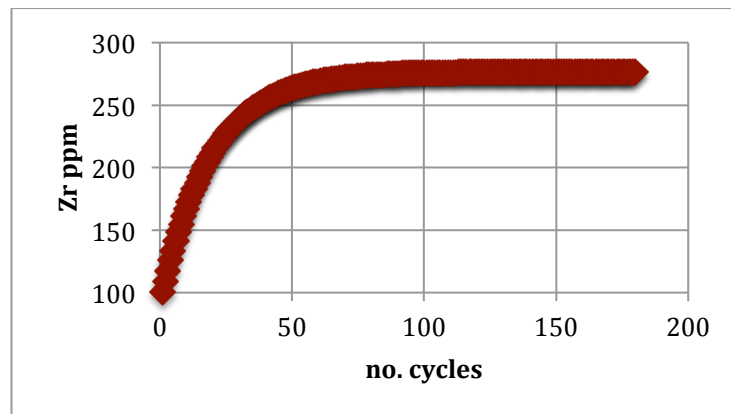
5.4 Assimilation and Fractional Crystallization (AFC)

One way to model combined assimilation and fractional crystallization is to use **FRE concept with R as the assimilant**. However, the two processes typically take place simultaneously with crystallization providing the energy for assimilation and it is possible to **model this very neatly as a continuous process** using the method of DePaolo, 1981.
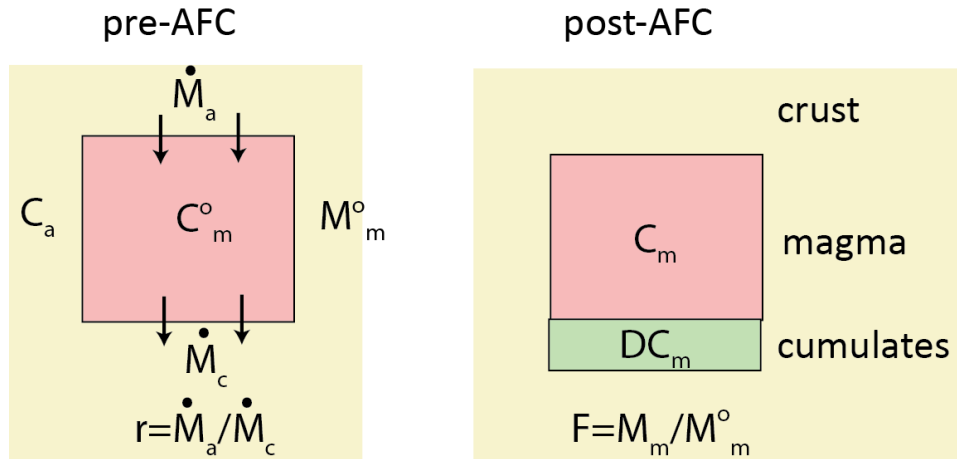
$$\frac{C_m}{C_o} = F^{-z} + \left[\frac{r}{r-1} \cdot \frac{C_a}{zC_o} \cdot (1 - F^{-z})\right]$$

$$\text{where } z = \frac{r+D-1}{r-1}$$

and **r** = rate of assimilation (M_a)/rate of fractional crystallization (M_c)

C_o and C_m = initial and final concentration of the trace element

C_a = concentration of the trace element in the assimilated crust

D = the bulk distribution coefficient of the trace element

M_o and M_m = initial and final mass of magma

F = mass fraction of magma remaining = M_m/M_o

Dots above masses indicate rates

5.4.1 AFC Modelling

The key to carrying out the modeling is **breaking down the complex equation to reduce errors**. The grid below shows the recommended approach (taking Rb as an example). The **variables are placed in a separate area** along **with z, which is calculated from D and r**. For a range of values of F, the component parts are then **combined and multiplied by C_o** to give the melt concentration.

	Rb
C_o	7
r	0.3
D	0.1
C_a	160
z	0.86

F	F^-z	r/(r-1)	C_a/zC_o	1-F^-z	C_m
1	1.00	-0.43	26.67	0.00	7.00
0.9	1.09	-0.43	26.67	-0.09	15.2
0.8	1.21	-0.43	26.67	-0.21	25.3
0.7	1.36	-0.43	26.67	-0.36	38.1
0.6	1.55	-0.43	26.67	-0.55	54.8
0.5	1.81	-0.43	26.67	-0.81	77.6
0.4	2.19	-0.43	26.67	-1.19	111
0.3	2.81	-0.43	26.67	-1.81	164
0.2	3.97	-0.43	26.67	-2.97	266
0.1	7.20	-0.43	26.67	-6.20	546

The example below is an **AFC model for volcanism in eastern Turkey** (Pearce et al., 1990) with r increasing from 0 to 0.7. The samples follow a **trend from uncontaminated magmas towards an upper crust contaminant** with values of r (rate of contamination relative to rate of fractional crystallization) from 0 to 0.7 (0, 0.025, 0.5, then 1-7). The trends are between possible primary magma 2362 and average Anatolian upper crust (UC).

Mus - Nemrut - Tendurek (b)
(Pearce et al., 1990)

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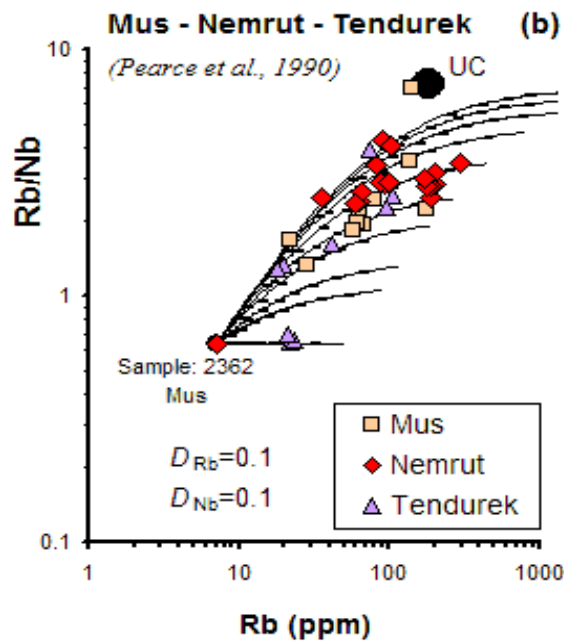
5.5 Energy-constrained Recharge-Assimilation-Fractional Crystallization (EC-RAFC)
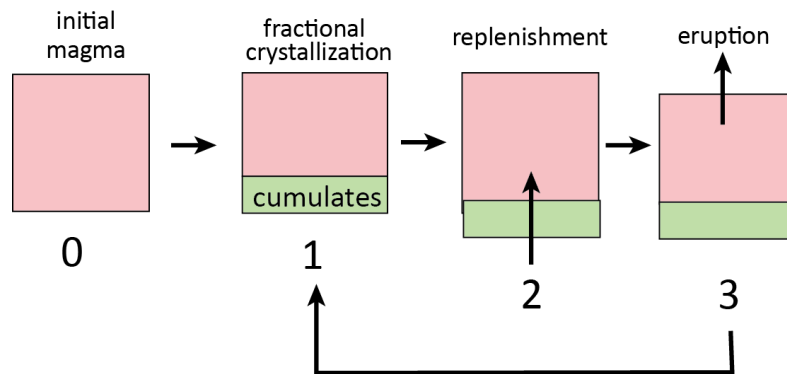
This is the same concept as RFC but incorporates assimilation and deals with the constraint of energy balance by incorporating the temperatures of country rock and magmas as well as latent heats of crystallization and fusion to ensure energy balance. This is beyond the scope of this course, but see https://earthref.org/EC-RAFC/. Key references are Spera & Bohrson (2001), Bohrson and Spera (2001) and Fowler et al. (2004). The conceptual diagram from Spera and Bohrosn (2001) is reproduced below.
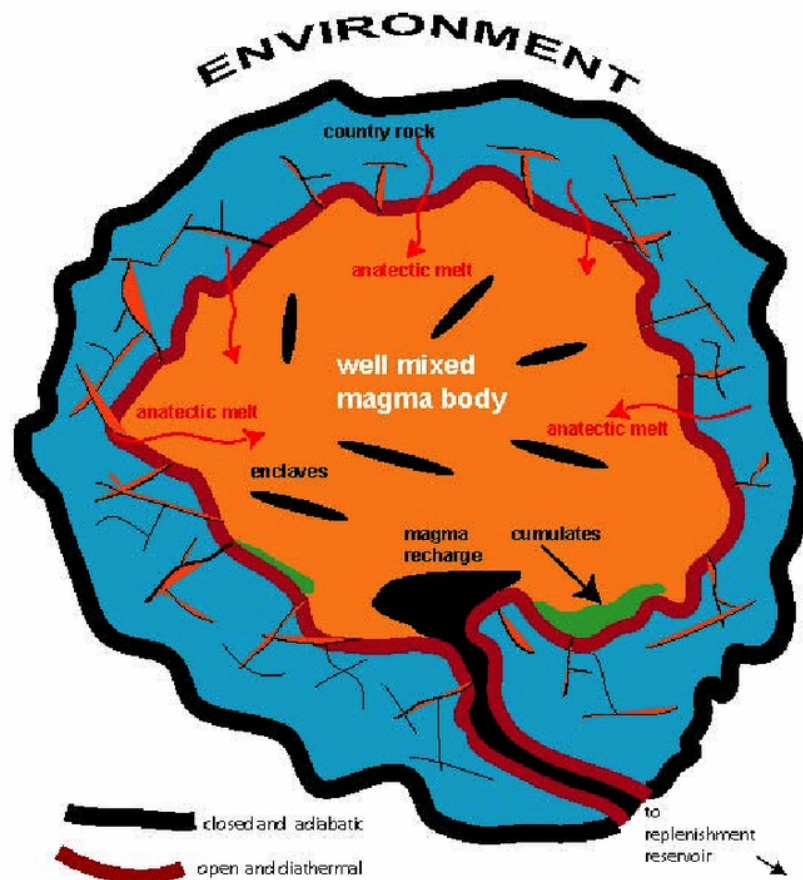
6. Practical: Modelling Magma Chamber Processes Using EXCEL

6.1 Mixing Exercises

Task 1, Open a new worksheet and label it **"Mixing".** Your aim is to repeat the mixing model in Section 4.1.

Task 2. Enter the grid below, which contains the basic data for mixing of a basalt and rhyolite magma. **Fill in the missing information for the elements, La, Sm, Tb and Yb**, using the mass balance equation from Section as reproduced below:

$$C_{mix} = X_{rhy}C_{rhy} + (1 - X_{rhy})C_{bas}$$

Check your element concentrations against the grid in Section 4.1.

	X_{rhy}	La	Sm	Tb	Yb	La/Yb	Tb/Yb
basalt	0	15	10	10	10		
	0.1						
	0.2						
	0.3						
	0.4						
	0.5						
	0.6						
	0.7						
	0.8						
	0.9						
rhyolite	1	100	50	20	10		

Task 3. Calculate the ratios La/Yb and Tb/Yb and so fill the last two columns of the grid.

Then **plot the mixing trend of La/Yb v Tb/Yb** and check against the plot in Section 4.2. Note that the common denominator (Yb) makes the trend a straight line.

6.2 Fractional Crystallization Exercises

Task 1. Return to your first spreadsheet and **set up a new worksheet entitled "Fr Xn".** The aim here is to draw a fractional melting trend for Sr against Zr in basic magmas with vectors for the different individual minerals and for a bulk mineral assemblage.

Task 2. Set up two grids containing the Sr v Zr data and **determine the missing value for D, and the missing values for C_l** using the Raleigh Fractionation equation (below). Check the answer for the upper grid against the grid in Section 5.1.1.

$$\frac{C_l}{C_o} = F^{D-1}$$

	X_i	K_i (Sr)	C_o(F=1)	C_l (F=0.75)	C_l (F=0.5)
olivine	0.2	0.01	300		
clinopyroxene	0.3	0.2	300		
plagioclase	0.5	2	300		
		D(Sr)			
ol+cpx+pl			300		

	X_i	K_i (Zr)	C_o(F=1)	C_l (F=0.75)	C_l (F=0.5)
olivine	0.2	0.01	200		
clinopyroxene	0.3	0.15	200		
plagioclase	0.5	0.02	200		
		D (Zr)			
ol+cpx+pl			200		

Task 3. Plot vectors for the individual minerals and bulk mineral assemblage using a log-log plot of Sr against Zr. Check your plot against the plot in Section 5.1.1.

6.3 Recharge and Fractional Crystallization (RFC) Exercises

Task 1. Return to your first spreadsheet and **set up a new sheet entitled "R-AFC".** The aim here is to reproduce the RFC model for the evolving Zr concentration in a magma chamber using RFC modeling.

Task 2. The grid below is taken from Section 5.3.1 but with the results of the calculations missing and some hints on how to calculate the concentrations in each cell. **Complete the grid using the methodology from Section 5.3.** Check the values against the completed grid in Section 5.3.1. Then extend the grid until the composition reaches its steady state.
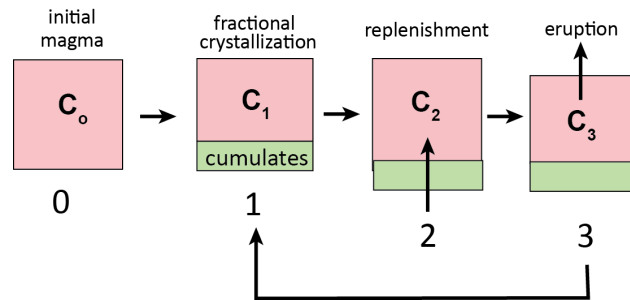
C_o to C_1 ($first\ fr.Xn\ event$): $C_1 = C_o F^{D-1}$

C_1 to C_2 ($recharge$): $C_2 = \dfrac{FC_1 + IC_o}{F + I}$

C_2 to C_3 ($eruption$): $C_3 = C_2$

C_3 to next cycle C_1 ($subsequent\ fr.Xn\ events$. $C_1' = C_3 F^{D-1}$

Co	100.00
D	0.04
F	0.90
I	0.15
E	0.05

	Magma	**C$_i$**	**C$_2$**	**C$_3$**
cycle	**Comp.**	**Fr Xn**	**Replen.**	**Eruption**
1	$=C_o$	$=C_o$ to C_1	$=C_1$ to C_2	$=C_2$ to C_3
2	$=C_3$ (cy1)	$=C_3$ to C_1	$=C_1$ to C_2	$=C_2$ to C_3
3	$=C_3$ (cy2)	$=C_3$ to C_1	$=C_1$ to C_2	$=C_2$ to C_3
4				
5				
6 etc				

Task 3. Plot the graph of Zr against the number of cycles to see how the value converges to a steady state composition. Check it against the plot in Section 5.3.2.

Task 4. Experiment by varying F, E, I and D and see how the concentration of Zr changes as the magma chamber evolves.

6.4 Assimilation and Fractional Crystallization (AFC) Exercises

Task 1: Open a new worksheet and label it **"AFC".** Your aim is to repeat the mixing model in Section 5.4.

Task 2: Below is the grid used in Section 5.4 to model the AFC process for Rb with the calculated values missing. **Complete the grid yourself and check for errors** against the full grid in Section 5.4. Don't forget to multiply the components by C_o.

	Rb
C_o	7
r	0.6
D	0.1
C_a	160
z	

F	F^-z	r/(r-1)	C_a/zC_o	1-F^-z	Cm
1					
0.9					
0.8					
0.7					
0.6					
0.5					
0.4					
0.3					
0.2					
0.1					

The equations are reproduced below. Of course, you can write it in EXCEL as one equation if you wish: in that case, just input the value for z and fill in the C_m column without the intermediate steps.

$$\frac{C_m}{C_o} = F^{-z} + \left[\frac{r}{r-1} \cdot \frac{C_a}{zC_o} \cdot (1 - F^{-z}) \right]$$

$$\text{where } z = \frac{r + D - 1}{r - 1}$$

Task 3. If you wish, you can also **reproduce the Rb/Nb v Rb diagram in Section 5.4.1**. To do this, copy and paste the Rb grid alongside the existing grid and edit it so that it has the values for Nb (C_o=10; D=0.1; C_a=20). Then add a column to the Rb grid with Rb/Nb and make the plot for one or more chosen values of r. Check it against the original diagram

7. References [optional reference material and for future use; not assessed]

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