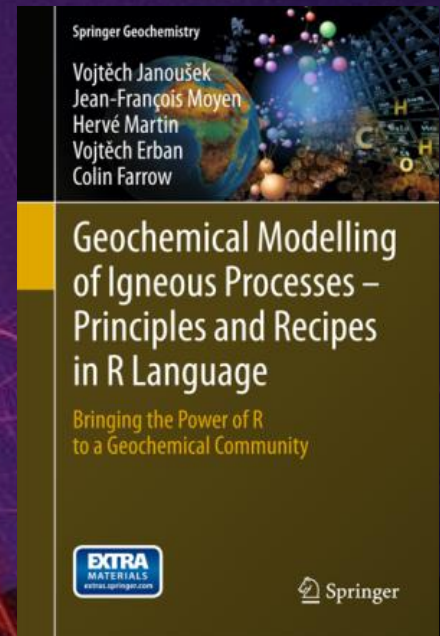




Vojtěch Janoušek

**Dealing with mixtures:
interpretation of major-
element data from igneous
rocks**





Major vs. trace elements, units of measurement

	ZV14	ZV85	ZV10
<i>Major element oxides (wt %)</i>			
SiO ₂	48.91	45.26	45.26
TiO ₂	0.45	0.33	0.29
Al ₂ O ₃	9.24	6.74	6.07
Fe ₂ O ₃	2.62	2.13	1.68
FeO	8.90	8.66	8.70
MnO	0.18	0.17	0.17
MgO	15.32	22.98	26.21
CaO	9.01	6.94	6.41
Na ₂ O	1.15	0.88	0.78
K ₂ O	0.08	0.05	0.04
P ₂ O ₅	0.03	0.02	0.02
S	0.04	0.05	0.05
H ₂ O+	3.27	3.41	2.20
H ₂ O-	0.72	0.57	0.28
CO ₂	0.46	0.84	1.04
Total	100.38	99.03	99.20

	ZV14	ZV85	ZV10
<i>Selected trace elements (ppm)</i>			
Ni	470	1110	1460
Cr	2080	2770	2330
V	187	140	118
Y	10	6	6
Zr	21	16	14
Rb	3.38	1.24	1.38
Sr	53.3	32.6	31.2
Ba	32	12	10
Nd	2.62	1.84	2.31
Sm	0.96	0.68	0.85
<i>Radiogenic isotope ratios</i>			
εNd	+2.4	+2.4	+2.5
⁸⁷ Sr/ ⁸⁶ Sr	0.7056	0.70511	0.70501
<i>Stable isotope ratios (‰)</i>			
δ ¹⁸ O	+7.3	+7.0	+6.8

Major-elements

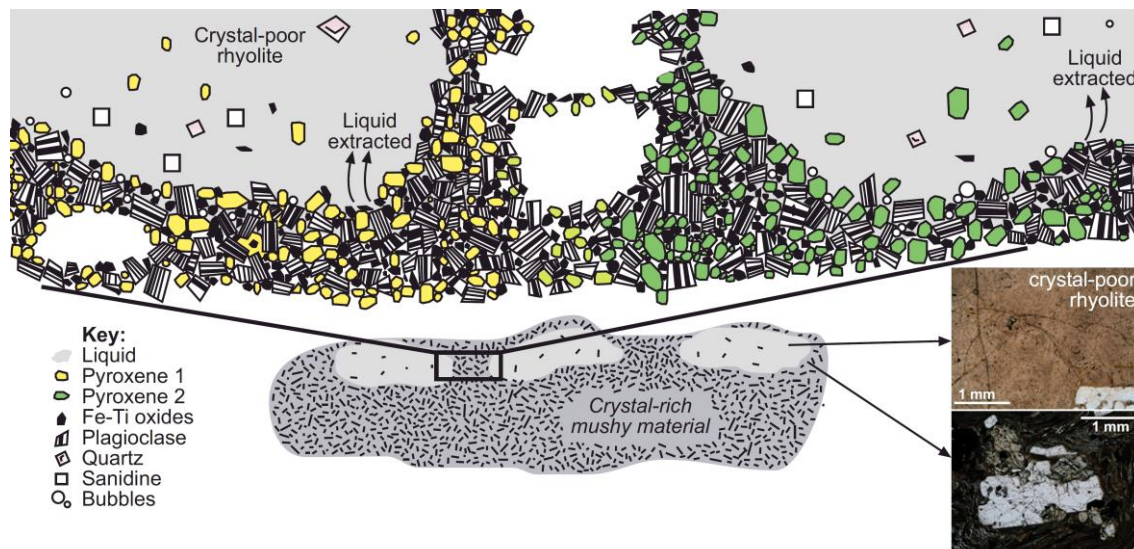
- **wt. % of oxides**
(comes from the days of wet chemistry analysis)

Trace elements

- **ppm, ppb, ppt**
(by weight)



Fractional crystallization



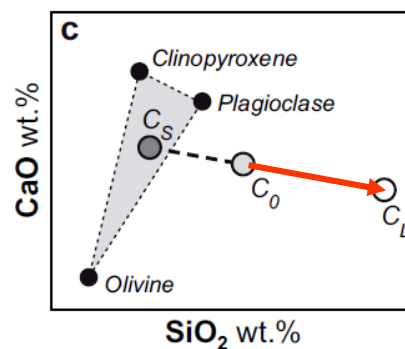
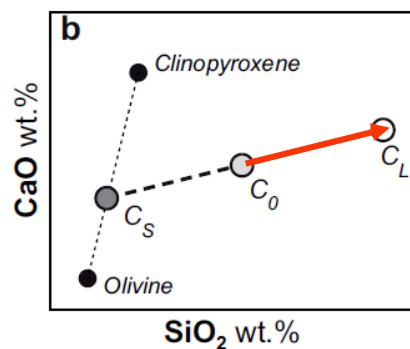
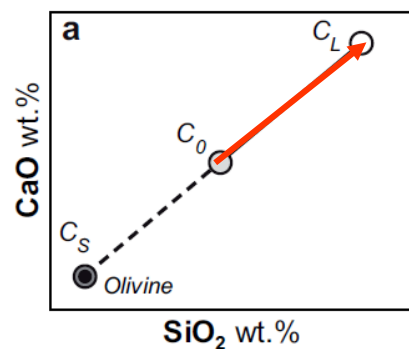
Simplified from:

ELLIS, B. S.,
BACHMANN, O. &
WOLFF, J. A., 2014.

Cumulate fragments in
silicic ignimbrites: The
case of the Snake River
Plain. *Geology*, **42**, 431–
434.

Liquid [0, L]

Solid
cumulate [S]






8.5: Generalized mixing

Table contains compositions of three ideal rock-forming minerals making up a model olivine gabbro:

wt. %	SiO ₂	Al ₂ O ₃	FeOt	MgO	CaO	Na ₂ O
Pl	50.54	31.70	0.00	0.00	14.36	3.40
Ol	39.19	0.00	18.75	42.06	0.00	0.00
Di	55.49	0.00	0.00	18.61	25.90	0.00



 `gabbro_modal.data`

- Calculate whole-rock geochemical composition of gabbro that contains 50 % Pl, 30 % Ol and 20 % Di by weight.

<https://www.virtualmicroscope.org/content/olivine-gabbro-huntly>



8.5: Generalized mixing

This is a simple calculation leading to a matrix multiplication of a vector with mineral proportions (m) by a matrix of mineral compositions (C_c) stored in the datafile.

$$\overrightarrow{C_s} = \begin{pmatrix} C_s^{SiO_2} \\ C_s^{Al_2O_3} \\ \vdots \\ C_s^{Na_2O} \end{pmatrix}$$

$$\overline{\overline{C_c}} = \begin{pmatrix} C_{Pl}^{SiO_2} & C_{Ol}^{SiO_2} & C_{Di}^{SiO_2} \\ C_{Pl}^{Al_2O_3} & C_{Ol}^{Al_2O_3} & C_{Di}^{Al_2O_3} \\ \vdots & \vdots & \vdots \\ C_{Pl}^{Na_2O} & C_{Ol}^{Na_2O} & C_{Di}^{Na_2O} \end{pmatrix}$$

$$\overrightarrow{m} = \begin{pmatrix} m_{Pl} \\ m_{Ol} \\ m_{Di} \end{pmatrix}$$

$$\overrightarrow{C_s} = \overline{\overline{C_c}} \times \overrightarrow{m} \sim \text{Eq. [6.14]}$$

Matrix multiplication in R is implemented via the `%*%` operator.



8.2: Fractional crystallization (direct)

Table contains analyses of Sázava tonalite (Janoušek et al. 2004) and some of its rock-forming minerals (Janoušek et al. 2000):

wt. %	Tonalite	Pl	Bt	Amp
SiO ₂	55.09	53.41	35.32	45.35
TiO ₂	0.75	0	2.11	1.39
Al ₂ O ₃	17.59	29.48	15.31	9.47
FeOt	7.73	0.09	23.56	18.57
MgO	3.52	0	9.05	9.82
CaO	8.2	11.27	0.01	11.92
Na ₂ O	2.83	5.05	0.1	1.08
K ₂ O	2.04	0.12	9.81	1.02



sazava_fc.data

- Calculate the composition of residual melt after 20% fractional crystallization of a cumulate consisting of 50 % Pl, 30 % Bt and 20 % Amp by weight.
- What is the composition of the cumulate?



8.2: Fractional crystallization (direct)

For each element j in the unfractionated/primitive magma (C_0), fractionated magma (C_L) and the crystallizing cumulate (C_S) can be written a mass-balance equation [Eq. 6.6]:

$$C_0^j = (1 - F_c) C_L^j + F_c C_S^j$$

Where degree of fractionation (F_c) is related to the mass fraction of melt (F) in the system:

$$F_c = (1 - F)$$

And also:

$$C_S^j = \sum_{i=1}^n (m_i c_i^j) \quad \text{Eq. [6.8]}$$

$$\vec{C}_s = \overline{\overline{C}}_c \times \vec{m}$$

$$\sum_{i=1}^n m_i = 1$$

$$C_L^j = \frac{C_0^j - C_S^j F_c}{(1 - F_c)} \quad \text{Eq. [8.2]}$$



9.4: “Normative” calculations (reversed Ex. 8.5)

wt. %	gabbro	Pl	Ol	Di
SiO ₂	48.125	50.54	39.19	55.49
Al ₂ O ₃	15.85	31.7	0	0
FeO	5.625	0	18.75	0
MgO	16.34	0	42.06	18.61
CaO	12.36	14.36	0	25.9
Na ₂ O	1.7	3.4	0	0

 `gabbro_modal2.data`

- Given the analyses of a gabbro and its mineral constituents (Table), estimate the wt. % of individual minerals using the least-square method.



9.4: “Normative” calculations (reversed Ex. 8.5)

Defining

(C_s = crystallizing cumulate, C_L = fractionated magma, C_0 = unfractionated/primitive magma, m = mass proportions of minerals in the cumulate):

$$\overrightarrow{C_s} = \begin{pmatrix} C_s^{SiO_2} \\ C_s^{Al_2O_3} \\ \vdots \\ C_s^{Na_2O} \end{pmatrix}$$

$$\overline{\overline{C_c}} = \begin{pmatrix} C_{Pl}^{SiO_2} & C_{Ol}^{SiO_2} & C_{Di}^{SiO_2} \\ C_{Pl}^{Al_2O_3} & C_{Ol}^{Al_2O_3} & C_{Di}^{Al_2O_3} \\ \vdots & \vdots & \vdots \\ C_{Pl}^{Na_2O} & C_{Ol}^{Na_2O} & C_{Di}^{Na_2O} \end{pmatrix}$$

$$\overrightarrow{m} = \begin{pmatrix} m_{Pl} \\ m_{Ol} \\ m_{Di} \end{pmatrix}$$

Allows a matrix formulation of:

$$\overrightarrow{C_s} = \overline{\overline{C_c}} \times \overrightarrow{m} \sim \text{Eq. [6.14]}$$

That can be solved for \overrightarrow{m} by the least-squares method.



9.4: “Normative” calculations (reversed Ex. 8.5)

In R the least-squares method is implemented by the function `lsfit` setting `intercept = FALSE`, so that the model passes through the origin.

$$\overrightarrow{C}_S^* = \overline{\overline{C}}_C \times \overrightarrow{m}^*$$

The value of mean squared residuals (R^2) represents an useful measure for goodness of fit:

$$R^2 = \left| \overrightarrow{C}_S^* - \overline{\overline{C}}_S \right|^2 = \min.$$



9.1: Fractional crystallization (reversed Ex. 8.2)

wt. %	tonalite	dif. magma	Pl	Bt	Amp
SiO ₂	55.09	57.270	53.41	35.32	45.35
TiO ₂	0.75	0.710	0	2.11	1.39
Al ₂ O ₃	17.59	16.681	29.48	15.31	9.47
FeOt	7.73	6.956	0.09	23.56	18.57
MgO	3.52	3.230	0	9.05	9.82
CaO	8.2	8.245	11.27	0.01	11.92
Na ₂ O	2.83	2.845	5.05	0.1	1.08
K ₂ O	2.04	1.748	0.12	9.81	1.02



sazava_fc2.data

- Given the compositions of the parental magma (tonalite), differentiated melt and crystallizing minerals (Table), estimate (by the least-square method) the degree of fractional crystallization and mineral proportions in the cumulate.



9.1: Fractional crystallization (reversed Ex. 8.2)

Setting

(C_0 = unfractionated/primitive magma, C_L = fractionated magma, C_{Pl} , C_{Bt} , C_{Amp} = mass proportions of plagioclase, biotite, amphibole in the crystallizing cumulate, F = melt fraction left in the system, m = mass proportions of minerals in the cumulate):

$$\begin{aligned} \overrightarrow{C_0} &= \begin{pmatrix} C_0^{SiO_2} \\ C_0^{TiO_2} \\ \vdots \\ C_0^{K_2O} \end{pmatrix} & \overline{C} &= \begin{pmatrix} C_L^{SiO_2} C_{Pl}^{SiO_2} & C_{Bt}^{SiO_2} & C_{Amp}^{SiO_2} \\ C_L^{TiO_2} C_{Pl}^{TiO_2} & C_{Bt}^{TiO_2} & C_{Amp}^{TiO_2} \\ \vdots & \vdots & \vdots \\ C_L^{K_2O} C_{Pl}^{K_2O} & C_{Bt}^{K_2O} & C_{Amp}^{K_2O} \end{pmatrix} & \overrightarrow{f'} &= \begin{pmatrix} (F) \\ (1-F)m_{Pl} \\ (1-F)m_{Bt} \\ (1-F)m_{Amp} \end{pmatrix} \end{aligned}$$

Allows a matrix formulation:

$$\overrightarrow{C_0} = \overline{C} \times \overrightarrow{f'}$$

Eq. [6.27]

That can be solved for $\overrightarrow{f'}$ by the least-squares method.