1 (i) $\delta^{18}O_{SMOW}$ of Pyroxene = 7 ‰

$$\delta^{18}O_{SMOW} = \left(\frac{(^{18}O/^{16}O)_{pyroxene}}{(^{18}O/^{16}O)_{SMOW}} - 1 \right) \times 1000 = 7$$

so $$\frac{(^{18}O/^{16}O)_{px}}{(^{18}O/^{16}O)_{SMOW}} = 1.007$$

so $$(^{18}O/^{16}O)_{px} = 1.007 \times (^{18}O/^{16}O)_{SMOW}$$

$$= 1.007 \times 0.0020052$$

$$= 0.00201924$$

likewise $$(^{18}O/^{16}O)_{plag} = 1.0077 \times (^{18}O/^{16}O)_{SMOW}$$

$$= 1.0077 \times 0.0020052$$

$$= 0.00202064$$

difference is 1 in the 6th place

(actually 1.4 ppm)

2(ii) $$\delta^{18}O_{snow-SMOW} = \left(\frac{0.001925}{0.0020052} - 1 \right) \times 1000$$

$$= -40.0 ‰$$ relative to SMOW

$$\delta D_{snow-SMOW} = \left(\frac{.00010747}{.00015576} - 1 \right) \times 1000$$

$$= -310 ‰$$ relative to SMOW

1 (iii) $\delta^{18}O_{coral-SMOW} = 26‰$

$$\Rightarrow \left(\frac{(^{18}O/^{16}O)_{coral}}{(^{18}O/^{16}O)_{SMOW}} - 1 \right) \times 1000 = 26‰$$

$$\Rightarrow \frac{(^{18}O/^{16}O)_{coral}}{(^{18}O/^{16}O)_{SMOW}} = 1.026$$

$$\Rightarrow (^{18}O/^{16}O)_{coral} = 1.026 \times 0.0020052$$

$$= 0.0020573$$

1 (iv) As above,

$$(^{18}O/^{16}O)_{PDB} = 1.0309 \times 0.0020052$$

$$= 0.0020672$$

So $$\delta^{18}O_{Coral-PDB} = \left(\frac{(^{18}O/^{16}O)_{coral}}{(^{18}O/^{16}O)_{PDB}} - 1 \right) \times 1000$$

$$= \left(\frac{.0020573}{.0020672} - 1 \right) \times 1000$$

$$= (0.99525 - 1) \times 1000$$

$$= (-0.0048) \times 1000$$

$$= -4.8‰$$

$$\delta^{18}O_{PDB-SMOW} + \delta^{18}O_{coral-PDB} = 30.9‰ - 4.8‰$$

$$= 26.1‰$$

whereas $\delta^{18}O_{coral-SMOW} = 26.0‰$

difference in δ values of magnetite and quartz as the "oxygen isotopic fractionation" between them. The following exercise will help you understand the relationship between α and δ values and how we can put measurements of $\delta^{18}O$ to work to estimate equilibration temperatures:

Famous geochemist Bob Clayton runs some experiments in which he synthesizes magnetite plus quartz at various temperatures. He separates the two minerals from the reaction products and measures their $\delta^{18}O$ values relative to the SMOW standard. He gets the following results:

T °C	T K	$10^6/T^2$	$\delta^{18}O_{qtz\text{-}SMOW}$	$\delta^{18}O_{mt\text{-}SMOW}$	$\alpha_{qtz\text{-}mt}$	1000 ln α	$\delta^{18}O_{qtz}$ - $\delta^{18}O_{mt}$
500	773	1.674	+1.02	-9.16	1.01027	10.22	10.18 ‰
700	973	1.056	+0.64	-5.79	1.00647	6.45	6.43 ‰
900	1173	0.727	+0.45	-3.98	1.00445	4.44	4.43 ‰
1100	1373	0.530	+0.33	-2.91	1.00325	3.24	3.24 ‰

Calculate the exact value of the equilibrium constant α at each temperature and add it to the table. You will need to convert the $\delta^{18}O$ values to isotopic ratios. Take $(^{18}O/^{16}O)_{SMOW}$ = 0.0020052. Fill in the rest of the table . Compare the value of 1000 ln $\alpha_{qtz\text{-}mt}$ at each temperature to the difference between the δ values of the two minerals. What do you notice ?

Draw a plot of 1000 ln $\alpha_{qtz\text{-}mt}$ vs $10^6/T^2$ and draw a line through the data. Note that a plot of $\delta^{18}O_{qtz}$- $\delta^{18}O_{mt}$ would have given you essentially the same diagram.

Plots of this type allow you to predict the difference in δ values between minerals, fluids and gases in equilibrium. Any pair of substances give a line on the diagram. For example, the line for quartz-pyroxene would have approximately 1/3 the slope of the quartz-magnetite line. At any given temperature, the difference in $\delta^{18}O$ values between pyroxene and quartz will be ~1/3 as large as the difference in $\delta^{18}O$ values of magnetite and quartz.

We can use these kinds relationships to determine temperatures of equilibration:

2 (a) Table: $\left({}^{18}O/{}^{16}O\right)_{SMOW} = 0.0020052$

At $500°C = 773K$, $\frac{10^6}{T^2} = 1.674$

$$\delta^{18}O_{qtz\text{-}SMOW} = 1.02, \quad \text{so} \left(\frac{18O}{16O}\right)_{qtz} = 1.00102 \times 0.0020052 = 0.002007$$

$$\delta^{18}O_{mt\text{-}SMOW} = -9.16, \quad \text{so} \left(\frac{18O}{16O}\right)_{mt} = 0.99084 \times \text{"} = 0.0019868$$

$$\Rightarrow \alpha_{qtz\text{-}mt} = \frac{\left({}^{18}O/{}^{16}O\right)_{qtz}}{\left({}^{18}O/{}^{16}O\right)_{mt}} = 1.01027$$

$$1000 \ln \alpha_{qtz\text{-}mt} = 10.22$$

<u>cf</u> $\delta^{18}O_{qtz} - \delta^{18}O_{mt} = 1.02 - (-9.16) = 10.18$ ‰

BOTH RELATIVE TO SMOW

At $700°C = 973K$; $\frac{10^6}{T^2} = 1.056$

$$\delta^{18}O_{qtz\text{-}SMOW} = 0.64, \quad \text{so} \left({}^{18}O/{}^{16}O\right)_{qtz} = 0.0020065$$

$$\delta^{18}O_{mt\text{-}SMOW} = -5.79 \quad \text{so} \left({}^{18}O/{}^{16}O\right)_{mt} = 0.0019936$$

$$\alpha_{qtz\text{-}mt} = 1.00647$$

$$1000 \ln \alpha_{qtz\text{-}mt} = 6.45$$

<u>cf</u> $\delta^{18}O_{qtz} - \delta^{18}O_{mt} = 0.64 - (-5.79) = 6.43$ ‰

At $900°C$ = 1173 K ; $10^6/T^2$ = 0.727

$\delta^{18}O_{qtz-SMOW}$ = 0.45 ‰ $\Rightarrow \left(\frac{^{18}O}{^{16}O}\right)_{qtz}$ = 0.0020061

$\delta^{18}O_{mt-SMOW}$ = −3.98 ‰ $\left(\frac{^{18}O}{^{16}O}\right)_{mt}$ = 0.0019972

$\Rightarrow \alpha_{qtz-mt}$ = 1.004448

$1000 \ln \alpha_{qtz-mt}$ = 4.44

cf $\delta^{18}O_{qtz-SMOW} - \delta^{18}O_{mt-SMOW}$ = 0.45 − (−3.98) = 4.43

At $1100°C$ = 1373 K ; $10^6/T^2$ = 0.530

$\delta^{18}O_{qtz-SMOW}$ = 0.33 $\Rightarrow \left(\frac{^{18}O}{^{16}O}\right)_{qtz}$ = 0.0020059

$\delta^{18}O_{mt-SMOW}$ = −2.91 $\left(\frac{^{18}O}{^{16}O}\right)_{mt}$ = 0.0019994

α_{qtz-mt} = 1.00325

$1000 \ln \alpha_{qtz-mt}$ = 3.24

cf $\delta^{18}O_{qtz-SMOW} - \delta^{18}O_{mt-SMOW}$ = 0.33 − (−2.91) = 3.24

Regressing these gives:

$$\left(1000 \ln \alpha_{qtz\text{-}mt}\right) = 6.10 \left(\frac{10^6}{T^2}\right)$$

which we can read as:

$$\left(\delta^{18}O_{qtz\text{-}SMOW} - \delta^{18}O_{mt\text{-}SMOW}\right) = 6.10 \left(\frac{10^6}{T^2}\right)$$

A pair of oxygen isotope analyses, one on quartz and one on co-existing magnetite gives a value for T.

2b) (i) At 700°C ; $1000 \ln \alpha_{qtz\text{-}mt} = 6.45$

ie $\delta^{18}O_{qtz\text{-}SMOW} - \delta^{18}O_{mt\text{-}SMOW} \approx 6.45$ ‰

if $\delta^{18}O_{qtz\text{-}SMOW} = 10$ ‰ ; $10 - \delta^{18}O_{mt\text{-}SMOW} = 6.45$

$\Rightarrow \delta^{18}O_{mt\text{-}SMOW} \approx 3.55$ ‰

if $\delta^{18}O_{qtz\text{-}SMOW} = 15$ ‰ ; $\delta^{18}O_{mt\text{-}SMOW} = 8.55$ ‰

2b (ii) $\delta^{18}O_{qtz\text{-}SMOW} = 11.1‰$, $\delta^{18}O_{mt\text{-}SMOW} = 7.0‰$ } What temperature did they equilibrate at?

$$\Rightarrow \quad \delta^{18}O_{qtz\text{-}SMOW} - \delta^{18}O_{mt\text{-}SMOW} = 4.1‰$$

Using the approximation derived on the handout (and confirmed by filling in the values in the table)

$$\delta^{18}O_{qtz\text{-}SMOW} - \delta^{18}O_{mt\text{-}SMOW} \approx 1000 \ln \alpha_{qtz\cdot mt} \approx 4.1‰$$

And from our regression of the experimental data in the table

$$1000 \ln \alpha_{qtz\text{-}mt} = 6.10\left(\frac{10^6}{T^2}\right)$$

$$\Rightarrow \quad \frac{4.1}{6.10} = \frac{10^6}{T^2} = 0.672$$

$$\Rightarrow \quad T^2 = \frac{10^6}{0.672} = 1.488 \times 10^6$$

$$T = 1220 \text{ K}$$

$$= 948\ ^\circ C$$

(iii) Did the feldspar equilibrate its O isotope composition with qtz and magnetite at 948° C?

Given $\delta^{18}O_{qtz-SMOW} = 11.1$ ‰

$\delta^{18}O_{\text{~~plag~~ albite}-SMOW} = 10.45$ ‰

$$\delta^{18}O_{qtz-SMOW} - \delta^{18}O_{albite-SMOW} \approx 1000 \ln\alpha_{qtz-albite} = 0.65$$

From the qtz-albite thermometer equation, $T_{equil.}$ is given by

$$0.65 = 0.97 \left(\frac{10^6}{T^2}\right)$$

$$\Rightarrow \quad T^2 = \frac{0.97 \times 10^6}{0.65} = 1.492 \times 10^6$$

$$\Rightarrow \quad T = 1222 \text{ K}$$

$$= 949 \,^\circ C$$

.... the same T as indicated by quartz-magnetite isotopic compositions. Suggests qtz, mt and albite all came to O-isotope equilibrium at ~950°C.

(iv) In the vein assemblage

$$\delta^{18}O_{qtz-SMOW} - \delta^{18}O_{SMOW} = 4.1 - 2.25 = 1.85 \text{ ‰}.$$

Substituting for $1000 \ln\alpha_{qtz-albite}$;

$$1.85 = 0.97 \left(\frac{10^6}{T^2}\right)$$

$$\Rightarrow \quad T^2 = \frac{0.97 \times 10^6}{1.85} = 5.24 \times 10^5$$

$$T = 724\ K$$

$$= 451\ ^\circ C$$

Veins were emplaced during cooling of the granite.

(v) Bulk $\delta^{18}O_{SMOW}$ value of the granite is between 7.0 – 11.1‰ (NB magnetite is almost always the "lightest" (i.e. most ^{16}O-enriched) mineral in a rock, quartz is usually the "heaviest" (i.e. most ^{18}O-enriched).)

Bulk $\delta^{18}O_{SMOW}$ value of qtz-fsp veins is between 2.25 – 4.1‰

Bulk values are different, so the veins must have crystallised from a different source material to the granite.

(vi) $$1000 \ln \alpha_{qtz \cdot water} \approx \delta^{18}O_{qtz\ SMOW} - \delta^{18}O_{water-SMOW} = 4.1\left(\frac{10^6}{T^2}\right) - 3.7$$

Solve for $\delta^{18}O$ of water ...

$$4.1 - \delta^{18}O_{water-SMOW} = 4.1\left(\frac{10^6}{T^2}\right) - 3.7 \; ; \quad T = 451^\circ C$$

$\delta^{18}O_{qtz-SMOW}$

$$\delta^{18}O_{water-SMOW} = (4.1 + 3.7) - \frac{4.1 \times 10^6}{(724)^2}$$

$$= 7.8 - 7.8$$

$$\delta^{18}O_{water-SMOW} = 0.0 ‰$$

Similarly, $\delta^{18}O_{albite-SMOW} - \delta^{18}O_{water-SMOW} = 3.13\left(\frac{10^6}{T^2}\right) - 3.7$

$$\Rightarrow \delta^{18}O_{water-SMOW} = (2.25 + 3.7) - \frac{3.13 \times 10^6}{(724)^2}$$

$$= 5.95 - 5.97$$

$$= -0.02 ‰$$

Hence $\delta^{18}O_{water}$ indicated by both minerals ~~was~~

$$= 0.0 ‰$$

ie. the water isotopic composition is the <u>same</u> as SMOW - Standard mean ocean water.

(vii) This suggests the veins may have formed from a fluid in equilibrium with seawater