Experimental calibration of oxygen isotope fractionation between calcite and tremolite in the presence of a CO_2–H_2O fluid and a new data processing method for three phase systems

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In order to prevent any decomposition of calcite and tremolite oxygen isotope exchange experiments between these two minerals were performed in the presence of small amounts of a supercritical $CO_2 - H_2O$ fluid exactly within the $P - T - X_{CO_2}$ stability range of the assemblage tremolite plus calcite. As to be expected, equilibrium was not obtained in our exchange experiments. Therefore a data processing method for three -- phase systems was developed to extrapolate partial equilibrium data to equilibrium values.

For the oxygen isotope exchange between three phases the principle of mass conservation and the assumption of identical extent of exchange among companion runs (i.e. $b = const.$) leads to the following relation (Zheng *et al.*, 1994):

$$\frac{1}{b} = \frac{\delta^{18}O^i_A - \delta^{18}O^f_A}{\delta^{18}O^i_A - \delta^{18}O^e_A}$$

$$= \frac{X_B(\Delta^{18}O^i_{A-B} - \Delta^{18}O^f_{A-B})}{X_B(\Delta^{18}O^i_{A-B} - \Delta^{18}O^e_{A-B})}$$

$$\frac{+X_C(\Delta^{18}O^i_{A-C} - \Delta^{18}O^f_{A-C})}{+X_C(\Delta^{18}O^i_{A-C} - \Delta^{18}O^e_{A-C})} \qquad (1)$$

where i, f, and e refer to initial, final, and equilibrium. A, B, and C denote the three phases A, B, and C (e. g. calcite, tremolite, fluid phase). X_A, X_B, and X_C are the mole fraction of oxygen in phase A, B, and C.

Eq. (1) can be rewritten as:

$$b[X_B(\Delta^{18}O^i_{A-B} - \Delta^{18}O^f_{A-B})$$
$$+ X_C(\Delta^{18}O^i_{A-C} - \Delta^{18}O^f_{A-C})]$$
$$= X_B(\Delta^{18}O^i_{A-B} - \Delta^{18}O^e_{A-B})$$
$$+ X_C(\Delta^{18}O^i_{A-C} - \Delta^{18}O^e_{A-C}) \qquad (2)$$

Rearranging Eq. (2) gives:

$$\underbrace{X_B\Delta^{18}O^i_{A-B} + X_C\Delta^{18}O^i_{A-C}}_{y}$$

$$= b\ \underbrace{[X_B(\Delta^{18}O^i_{A-B} - \Delta^{18}O^f_{A-B})}_{x_1}$$

$$+ \underbrace{X_C(\Delta^{18}O^i_{A-C} - \Delta^{18}O^f_{A-C})]}_{x_2}$$

$$+ \underbrace{X_B\Delta^{18}O^e_{A-B} + X_C\Delta^{18}O^e_{A-C}}_{a} \qquad (3)$$

A short form of Eq. (3) is:

$$y = b(x_1 + x_2) + a \qquad (4)$$

If in a plot of y against x ($x = x_1 + x_2$) the experimental data points of a set of companion runs fit to a straight line the above assumption of $b = const.$ i. e. of an identical extent of exchange in all runs is proved (see Fig. 1). It is then possible to calculate the equilibrium fractionation between the phases A and B from the intercept a by the following relation [Eq. (3) and (4)]:

$$\Delta^{18}O^e_{A-B} = (a - X_C\Delta^{18}O^e_{A-C})/X_B \qquad (5)$$

For this calculation the equilibrium fractionation between A and C, $\Delta^{18}O^e_{A-C}$, has to be known.

Fig. 1 depicts the experimental results of three companion runs of calcite – tremolite oxygen isotope exchange performed in the presence of a small amount of a $CO_2 - H_2O$ fluid. The experimental value for the intercept a is 1.22 and $\Delta^{18}O^e_{calcite-fluid}$ for $X_{CO_2} = 0.2$ and $640° > C$ is -1.25 (Zheng *et al.*, 1994). With these figures and $X_{Fd} = 0.07$ and $X_{Tr} = 0.465$ (known from the experiments) one gets from Eq. (5) $\Delta^{18}O^e_{Cc-Tr(640°C)}$. The slope b of the line in Fig. (1) is 1.23 which corresponds to an exchange of 81%. By further experiments the oxygen isotope equilibrium fractionation between calcite and tremolite was determined also for the tempera-
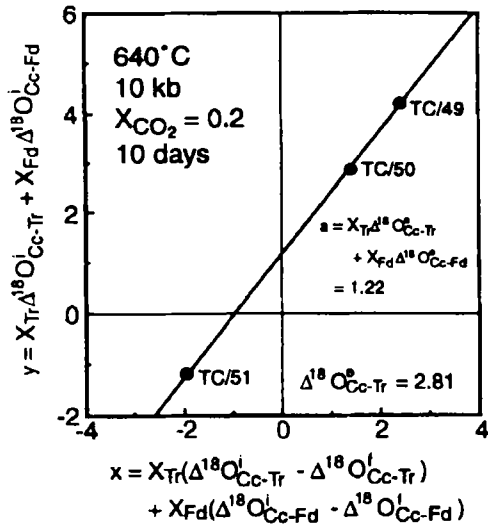
FIG. 1. Plot of experimental data for oxygen isotope exchange between calcite and tremolite in the presence of a $CO_2 - H_2O$ fluid, using the data processing method for a three phase system.

tures of 520°, 560°, 580°, and 680°C.

The results are depicted in Fig. 2 together with calculated data using modified increment methods (Zheng 1993 and Hoffbauer *et al.*, 1994). Good agreement exists between experimental and calculated eqilibrium data.

References

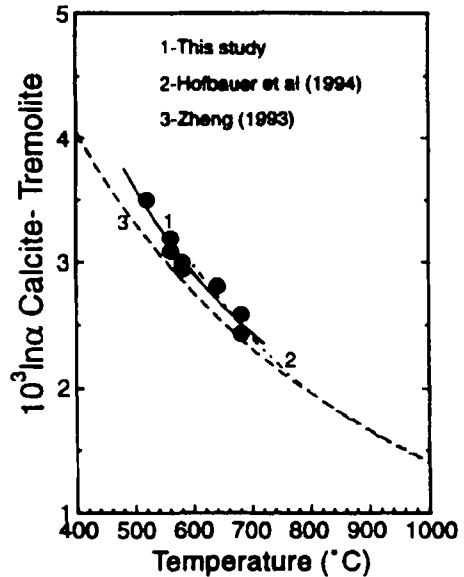Hoffbauer, R., Hoernes, S., Fiorentini, E. (1994)

FIG. 2. Comparison of equilibrium oxygen isotope fractionation between calcite and tremolite experimentally determined in this study with the theoretical calculations of Hoffbauer *et al.* (1994) and Zheng (1993).

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