

Oxygen isotopic thermometer calibrations

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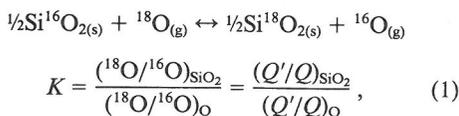
Abstract—The equilibrium oxygen isotopic fractionation between mineral *A* and mineral *B* can be expressed as the algebraic difference between two functions f_A and f_B , which are the logarithms of the reduced isotopic partition function ratios for the two minerals. A combination of laboratory experiment and statistical thermodynamic calculation is used to give these functions over a wide temperature range. For several major rock-forming minerals, the following polynomial expressions are good approximations for temperatures greater than 400 K:

$$\begin{aligned} \text{calcite } f_{Ca} &= 11.781x - 0.420x^2 + 0.0158x^3 \\ \text{quartz } f_{Qz} &= 12.116x - 0.370x^2 + 0.0123x^3 \\ \text{albite } f_{Ab} &= 11.134x - 0.326x^2 + 0.0104x^3 \\ \text{anorthite } f_{An} &= 9.993x - 0.271x^2 + 0.0082x^3 \\ \text{diopside } f_{Di} &= 9.237x - 0.199x^2 + 0.0053x^3 \\ \text{forsterite } f_{Fo} &= 8.326x - 0.142x^2 + 0.0032x^3 \\ \text{magnetite } f_{Mt} &= 5.674x - 0.038x^2 + 0.0003x^3 \end{aligned}$$

where $x = 10^6 T^{-2}$ (T in kelvins).

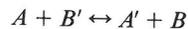
INTRODUCTION

OXYGEN ISOTOPIC FRACTIONATIONS among the major rock-forming minerals are useful for geologic thermometry and for modeling fluid-rock exchange processes. These applications require knowledge of the equilibrium fractionation factors for many mineral pairs over a broad range of temperatures. The fractionation factors are expressed most succinctly as differences between reduced partition function ratios for each mineral pair (UREY, 1947). The reduced partition function ratio is equivalent to the equilibrium constant for exchange of one isotopic atom between a mineral and an oxygen atom gas, *e.g.* for quartz



where Q and Q' are reduced partition functions for quartz, and the prime denotes the ^{18}O -substituted mineral. Thus, the quantities $\ln(Q'/Q)$ are proportional to the Gibbs Free Energy, and differences in

the values for any two phases at the same temperature give the equilibrium constant for isotopic exchange between those two phases:



$$\ln K_{AB} = \ln(Q'/Q)_A - \ln(Q'/Q)_B. \quad (2)$$

Values of Q'/Q can be determined by laboratory exchange experiments (*e.g.* CLAYTON *et al.*, 1989) or by statistical mechanical calculations (*e.g.* KIEFFER, 1982). Each method has advantages and disadvantages. The experimental method can produce results of high accuracy but only over limited ranges of temperature. The experiments are time-consuming, so that accumulation of results for a large number of minerals is slow. The calculations have no inherent temperature limitations, and can be applied to any phase for which adequate spectroscopic and mechanical data are available. However, they are limited in accuracy as a consequence of the approximations needed to carry out the calculations and the limited accuracy of the spectroscopic data. The purpose of this paper is to effect a combination of these two methods so as to achieve the advantages

of both. This is done by applying a small "adjustment factor" to the calculated partition function ratios so as to bring them into agreement with experiment. The modified partition function ratios can then be used to extrapolate to temperatures beyond the experimentally accessible range. It is found that simple polynomial expressions are adequate to express partition function ratios at all temperatures above 400 K.

The mineral calcite plays a key role in this approach. Over 90% of the isotopic partition function ratio for calcite arises from the internal vibrational modes of the carbonate ion, for which frequencies and isotopic frequency shifts are well known (KIEFFER, 1982; CHACKO *et al.*, 1991). For these modes, the carbonate ion can be treated almost as if it were gaseous, thus greatly enhancing the accuracy of the result. The remaining contributions to the partition function ratio, coming from the lattice vibrations of the crystal, have been estimated using two completely different sets of approximations (KIEFFER, 1982; CHACKO *et al.*, 1991), and agreement between the calculations is excellent. Thus, the calculated partition function ratios for oxygen in calcite are probably better known than those for oxygen in any other mineral.

Furthermore, experimental measurements have been made of oxygen isotopic fractionation between calcite and gaseous carbon dioxide (CHACKO *et al.*, 1991). Since the isotopic partition function ratios for CO₂ gas are very accurately known, the experiments provide an independent check on the accuracy of the calculated partition function ratios for calcite. The agreement is excellent for high-temperature exchange experiments (400–800°C), as well as for experiments at 0 and 25°C (CHACKO *et al.*, 1991).

Calcite can thus provide the link between accurate *theoretical* calculations for CO₂, and accurate *experimental* measurements of isotopic exchange between calcite and silicates (CLAYTON *et al.*, 1989; CHIBA *et al.*, 1989). Such calcite-silicate experiments have been done for quartz, albite, anorthite, diopside, and forsterite at temperatures in the range 600–1300°C. Calcite-magnetite fractionations have also been measured from 800 to 1200°C (CHIBA *et al.*, 1989).

COMPARISON OF THEORY AND EXPERIMENT

The isotopic partition function ratios of KIEFFER (1982) form the basis of this paper. However, because these were computed from a combination of Einstein and Debye functions representing different

frequency ranges of the crystal vibrations, the resulting data are not in a convenient analytical form. Ratios have been computed at intervals of 5 K from 325 to 1200 K, and at intervals of 500 K from 1500 to 4000 K. These were shown graphically by KIEFFER (1982). UREY (1947) and BIGELEISEN and MAYER (1947) showed that $\ln(Q'/Q)$ is asymptotically proportional to $1/T^2$ at high temperatures. This suggests that a polynomial in $1/T^2$ might be a good approximation to the curves over some temperature range. We have found empirically that a cubic function in $1/T^2$ fits the calculated results within ± 0.02 per mil for all temperatures from 400 K to infinity. Extension of the temperature range down to 300 K results in a much poorer fit: residuals increase by a factor of five. The constant term in all the cubic fits was found to be less than 0.01 and has been set equal to zero for convenience. A cubic function in $1/T$ fits almost as well as the $1/T^2$ function for most of the temperature range above 400 K but, as is expected, fits poorly at the highest temperatures.

The polynomial curve for each silicate mineral can then be combined with that for calcite to give a calculated calcite-silicate fractionation curve. This can be compared directly with the corresponding calcite-silicate experimental data. The results for calcite-anorthite and calcite-forsterite are shown in Figs. 1 and 2. In both cases, the experimental data conform to the calculated curves within the analytical uncertainty (which is rather large for anorthite). It is evident that a straight line through the origin would fit the data equally well, but the curvature of the plots shows that extrapolation of such a straight line to lower temperature would result in serious error.

Similar graphs for calcite-albite and calcite-diopside are shown in Figs. 3 and 4. The calculated calcite-albite curve lies about 0.1 per mil below the experimental points, and the calcite-diopside curve lies about 0.1 per mil above the experimental points. These small differences are well within the uncertainties which result from the necessary approximations of the calculations. A modified curve was obtained in each case by applying a multiplicative factor to the calculated partition function ratios for albite and diopside. The factors used were 0.994 and 1.008, respectively. That is, adjustments of less than 1% are needed to bring calculation and experiment into agreement. The rationale for a multiplicative correction comes from the fact that the isotopic fractionation is approximately proportional to terms of the form $\omega \cdot \Delta\omega$ (BIGELEISEN and MAYER, 1947), so that an error of 1% in the assignment of the vibrational frequency, ω , or its iso-

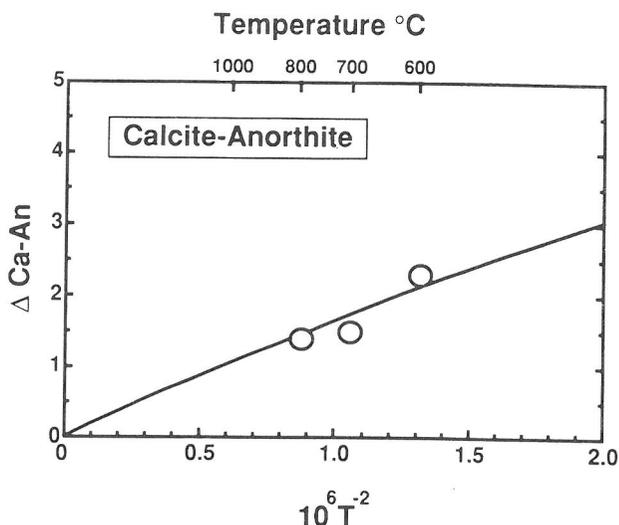


FIG. 1. Oxygen isotopic fractionation between calcite and anorthite. Experimental data points are from CLAYTON *et al.* (1989); theoretical curve is from KIEFFER (1982).

topic shift, $\Delta\omega$, results in a 1% error in the contribution of that vibrational mode to the partition function ratio.

The results for calcite-quartz were less satisfactory (Fig. 5). Two calculated curves are shown, one by KIEFFER (1982) and one recalculated from the vibrational frequencies determined by the lattice-dynamic treatment of KAWABE (1978). The Kawabe curve is a much better fit to the experimental data, and an excellent fit is achieved by use of an "adjustment factor" of 1.004.

Magnetite is an important mineral for oxygen isotope geochemistry, because it is usually the most

^{18}O -poor mineral in a rock and, thus, in combination with quartz or feldspar, gives the most sensitive geothermometer. Magnetite was not included in the calculations of KIEFFER (1982) because its opacity prevents adequate spectroscopic determination of its vibrational spectrum. An estimate of the magnetite partition function ratio was made by BECKER (1971), who used a combination of low-temperature heat capacity data for the acoustic modes and a single Einstein frequency to represent the unknown vibrational frequencies. The value of that frequency was chosen to fit the experimental magnetite-water fractionations of O'NEIL and

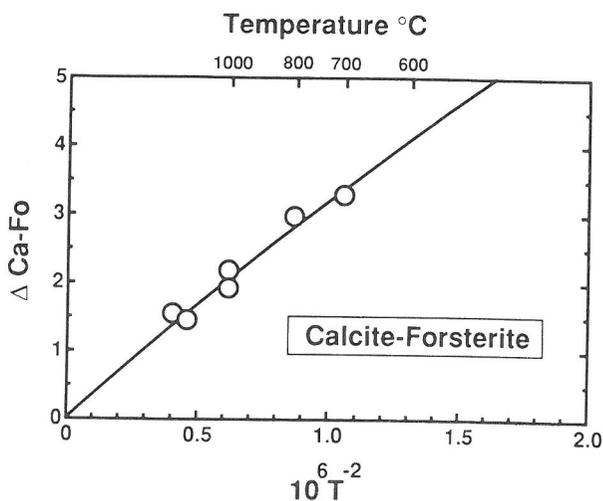


FIG. 2. Oxygen isotopic fractionation between calcite and forsterite. Experimental data points are from CHIBA *et al.* (1989); theoretical curve is from KIEFFER (1982).

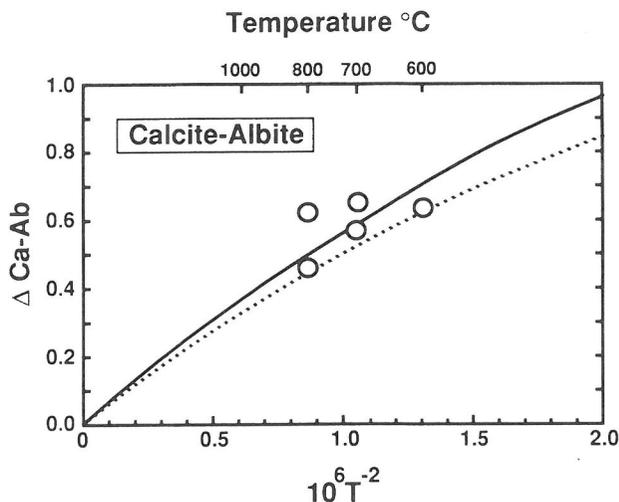


FIG. 3. Oxygen isotopic fractionation between calcite and albite. Experimental data points are from CLAYTON *et al.* (1989); theoretical curve (dashed line) is from KIEFFER (1982). Solid line is obtained by multiplying the Kieffer calculations for albite by 0.994 in order to fit the experimental data. Note expanded scale.

CLAYTON (1964) at 700 and 800°C. We have followed the same spirit in making a new estimate of the magnetite partition function ratio. The acoustic modes were represented by a Debye temperature of 585 K (as in BECKER, 1971) with an isotopic shift factor of 0.983123 (square root of the ratio of formula weights). The remaining degrees of freedom were represented by a set of identical Einstein functions with $\omega_{16} = 447 \text{ cm}^{-1}$, and an isotopic shift

factor of 0.964144, determined from the product rule (BECKER, 1971; KIEFFER, 1982). The frequency of 447 cm^{-1} was chosen to fit the calcite-magnetite experimental data of CHIBA *et al.* (1989). The resulting calcite-magnetite curve is shown in Fig. 6. The polynomial approximation of the magnetite partition function ratio is

$$f = 5.674x - 0.038x^2 + 0.0003x^3, \quad (3)$$

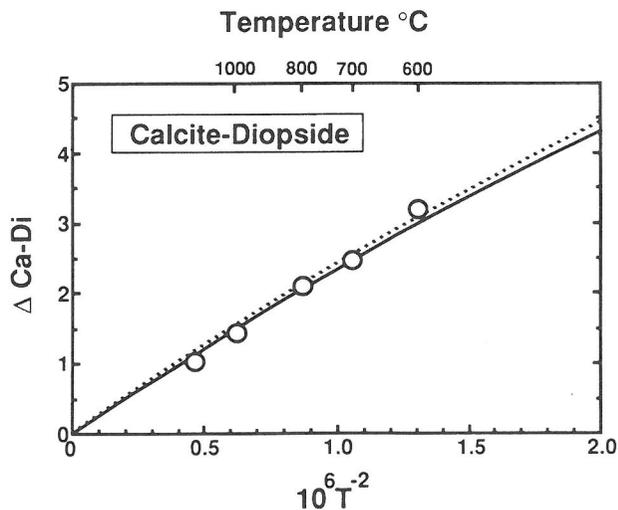


FIG. 4. Oxygen isotopic fractionation between calcite and diopside. Experimental data points are from CHIBA *et al.* (1989); theoretical curve (dashed line) is from KIEFFER (1982). Solid line is obtained by multiplying the Kieffer calculations for diopside by 1.008 in order to fit the experimental data.

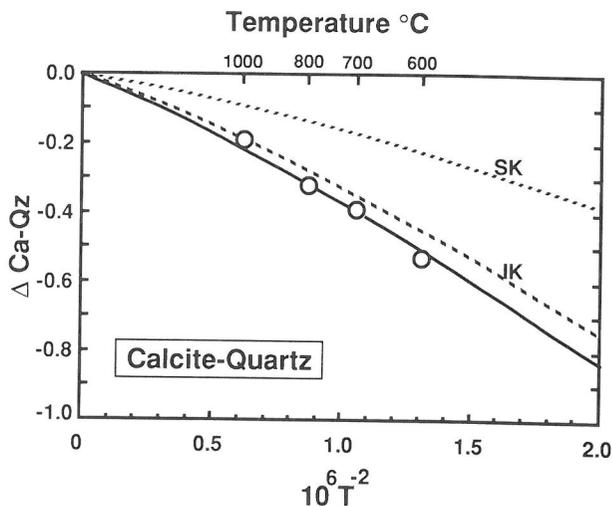


FIG. 5. Oxygen isotopic fractionation between calcite and quartz. Experimental data points are from CLAYTON *et al.* (1989); theoretical curves are from KIEFFER (1982) (dotted line SK) and recalculated from the data of KAWABE (1978) (dashed line IK). Solid line is obtained by multiplying the Kawabe recalculations for quartz by 1.004 in order to fit the experimental data. Note expanded scale.

where $x = 10^6 T^{-2}$. This function is almost a straight line on a T^{-2} plot, as is expected for a phase with no high-frequency ($>1000 \text{ cm}^{-1}$) vibrations. The same property is seen in other oxides (KIEFFER, 1982).

The magnetite partition function ratios given here are 11% smaller than those of BECKER (1971) at all temperatures. This difference is due *entirely* to the different choice of experimental data used for curve fitting and is independent of minor details in the modeling. For purposes of isotopic thermometry, the result is to increase silicate-magnetite temperatures somewhat: the effect on quartz-magnetite temperatures is an increase of about 40°C over a wide temperature range.

The polynomial functions for the seven minerals considered here are given in Table 1. Previous fits to the same experimental data, valid only at high temperatures, were provided by simple one-parameter equations of the form

$$\Delta_{ij} = A_{ij} \times 10^6 T^{-2} \quad (4)$$

(CLAYTON *et al.*, 1989; CHIBA *et al.*, 1989), where Δ_{ij} is the fractionation between mineral i and mineral j . Thus, the fractionation at $T = 1000 \text{ K}$ is simply A . The present results can be compared with the previous ones by evaluating the polynomials at $T = 1000 \text{ K}$, as is done in Table 2. The results are almost identical, as is expected, since 1000 K is in the middle of the experimental temperature range

to which both sets of curves are tied. The advantage of the polynomial curves is that they allow extrapolation to temperatures hundreds of degrees below the experimental range.

Graphs of the polynomial functions for the reduced partition function ratios of individual minerals over an extended temperature range are shown in Fig. 7. The nearly linear portions of these graphs at temperatures $> 600^\circ\text{C}$ are determined by fitting the experimental data, whereas the curvatures at lower temperatures are determined by the statistical-mechanical calculations.

ERROR ESTIMATES

Uncertainties in the coefficients for the equations in Table 1 arise from several sources: analytical error in the experimental measurements, approximations in the assignment of vibrational frequencies and their isotopic shifts, neglect of anharmonicity effects, and the use of polynomial approximations. Errors in the experimental calcite-mineral fractionations have been estimated by CHIBA *et al.* (1989), based on the internal scatter of the data and the accuracy of isotopic measurements. They found little variation in the error from one system to another, with an average uncertainty in the coefficient A , in Eq. (4), of ± 0.10 (1σ standard error). The error in A is independent of the magnitude of A . In terms of the polynomial expressions used here, the coefficient A is determined by the *difference* in the curves for the

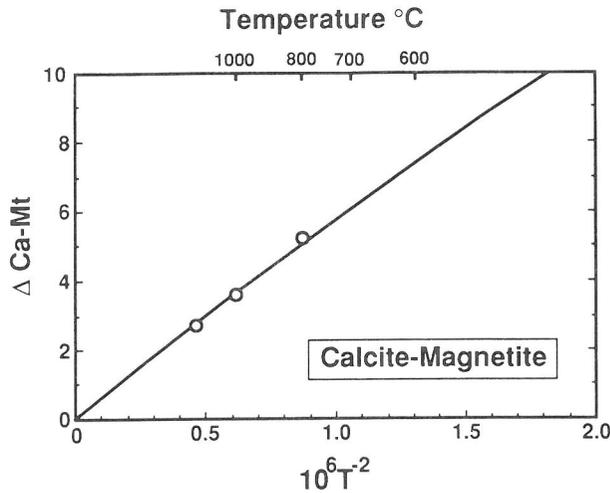


FIG. 6. Oxygen isotopic fractionation between calcite and magnetite. Experimental data points are from CHIBA *et al.* (1989). Curve is an empirical fit to the data based on a simple combination of Debye and Einstein functions for magnetite (see text).

two minerals involved, so that the absolute uncertainty in A can be partitioned between the two curves. Thus, the dominant term for calcite, $11.781 \times 10^6 T^{-2}$, has an uncertainty of about 0.07 at $T = 1000$ K, *i.e.* about 0.6%. Absolute uncertainties in the coefficient of x should be similar for other minerals, so that *relative* uncertainties range from 0.6% for quartz, calcite, and albite, to 1.2% for magnetite.

Errors introduced by the statistical mechanical calculations are significant only to the extent that they are not removed by tying the calculations to the experimental data. For example, an error of 5% in the assignment of a vibration frequency in quartz which is on the order of 500 cm^{-1} leads to an error of about 0.3% in the partition function ratio. However, this fractional error is virtually constant over all temperatures considered, and hence its effect is removed by the experimental normalization used. The same is not true for a higher-frequency vibration ($>1000 \text{ cm}^{-1}$), where a similar 5% error can

produce an error of 1.1% at 1000 K and 0.9% at 400 K. If the calculation is normalized to experimental data at 1000 K, the extrapolated partition function will be in error by 0.13 per mil at 400 K, an uncertainty which is still small compared to the errors in the experimental data used for normalization.

Effects of vibrational anharmonicity are necessarily neglected for solids since sufficiently accurate vibrational data are unavailable. Calculations with

Table 1. Partition function ratios for individual minerals*

Calcite	$f = 11.781x - 0.420x^2 + 0.0158x^3$
Quartz	$f = 12.116x - 0.370x^2 + 0.0123x^3$
Albite	$f = 11.134x - 0.326x^2 + 0.0104x^3$
Anorthite	$f = 9.993x - 0.271x^2 + 0.0082x^3$
Diopside	$f = 9.237x - 0.199x^2 + 0.0053x^3$
Forsterite	$f = 8.326x - 0.142x^2 + 0.0032x^3$
Magnetite	$f = 5.674x - 0.038x^2 + 0.0003x^3$

* f = reduced partition function ratio, as $1000 \ln(Q'/Q)$. $x = 10^6 T^{-2}$.

Table 2. Comparison of polynomial and linear fits for mineral pairs at 1000 K*

	Qz	Ab	An	Di	Fo	Mt
Ca	-0.38	0.56	1.65	2.33	3.19	5.74
	-0.38	0.56	1.61	2.37	3.29	5.91
Qz		0.94	2.03	2.72	3.57	6.12
		0.94	1.99	2.75	3.67	6.29
Ab			1.09	1.78	2.63	5.18
			1.05	1.81	2.73	5.35
An				0.69	1.54	4.09
				0.76	1.68	4.30
Di					0.86	3.41
					0.92	3.54
Fo						2.55
						2.62

* For each entry, a positive value indicates ^{18}O enrichment in the phase on the left. The upper entry is the fractionation at 1000 K based on the equations of Table 1; the lower entry is the value of A in the equations

$$\Delta = A \times 10^6 T^{-2}$$

of CHIBA *et al.* (1989).

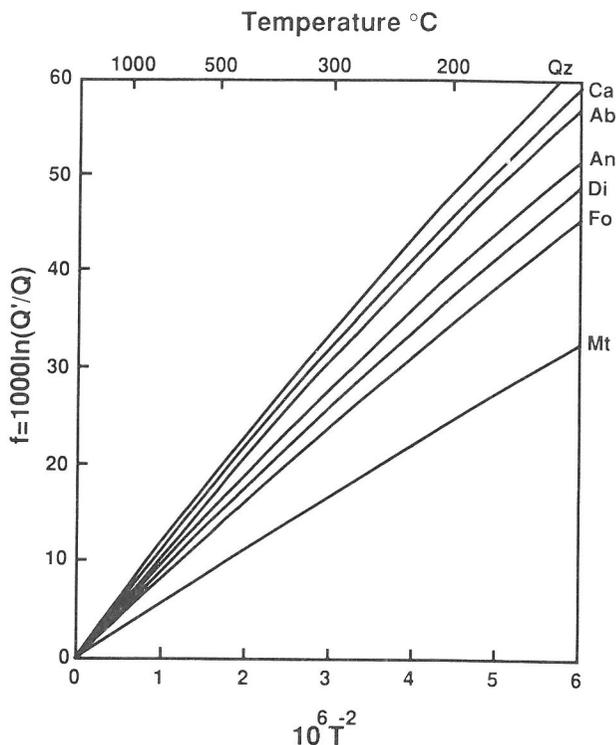


FIG. 7. Isotopic reduced partition function curves for the seven minerals discussed here. Mineral-pair isotopic fractionations are obtained by subtraction of one curve from another.

and without anharmonic corrections have been done for carbon dioxide, and show that the anharmonic correction is an almost constant fraction of the total partition function ratio at all temperatures, and its effect is thus removed in the experimental normalization used here.

Finally, the polynomial approximations have been found to fit the calculated partition functions of KIEFFER (1982) to better than ± 0.02 per mil for all temperatures above 400 K, and thus add no significant uncertainty to the analysis.

Of all the sources of error considered, that associated with the laboratory measurement of fractionation factors is much larger than the others. The final results are thus limited by the accuracy of the experiments. However, in assessing the accuracy of a particular isotopic thermometer, the functional dependence of Δ on T must be taken into account. For example, for the quartz-magnetite mineral pair, an uncertainty of 1.3% in the coefficients of the calibration equation produces an error in a temperature estimate of 7 K at 1000 K and 3 K at 400 K. These numbers can be compared with the effects of analytical uncertainty in the *rock data* to which the thermometer may be applied: an error

in the quartz-magnetite fractionation of 0.2 per mil gives an error in the temperature estimate of 17 K at 1000 K and 2 K at 400 K.

CONCLUSIONS

Oxygen isotopic fractionations among several major rock-forming minerals can be calculated from a set of polynomial expressions which are good approximations to the reduced partition function ratios for individual minerals for all temperatures above 400 K. These equations are excellent fits to the equilibrium fractionation factors measured in laboratory exchange experiments and permit extrapolation of those data to higher and lower temperatures, thus covering almost all the temperature range for which such isotopic partition function ratios are needed.

Other minerals may be added to this scheme as calculations and laboratory experiments become available. KIEFFER's (1982) calculations include muscovite, clinoenstatite, pyrope, grossular, andradite, zircon, and rutile, for which calcite exchange experiments can be carried out. It should be noted that, in principle, only one well-deter-

mined experimental point is sufficient to "calibrate" each theoretical curve. It is particularly desirable to include the garnet minerals because of their importance in metamorphic rocks.

Acknowledgements—This research was supported by National Science Foundation grant EAR 89 20584.

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