

Equilibrium garnet–calcite oxygen isotope fractionation

J.M. Rosenbaum
D.P. Matthey

Dept. of Earth Sciences, Univ. of Leeds, Leeds LS2 9JT UK.
Dept. of Geology, Royal Holloway - Univ. of London, Egham
TW20 0EX UK.

S. Elphick

Dept. of Geology and Geophysics, Univ. of Edinburgh, Edinburgh
EH9 3JW UK.

Introduction

We have determined the equilibrium oxygen isotope fractionation between grossularite and calcite from 800–1200°C at ~23 kbar. These data, when combined with published mineral-carbonate oxygen-isotope fractionation data (Clayton *et al.*, 1989; Chiba *et al.*, 1989), allow direct experimental calibration of oxygen isotope geothermometers involving garnet. As garnet is an important mineral in both metamorphic and igneous terrains (i.e. skarn, eclogite, garnet lherzolite), knowledge of oxygen partitioning behaviour between garnet and other common silicates will lead to a better understanding of the temperature history of these terrains.

Methods

Isotopically-characterized, finely-ground (<20m) natural grossularite and natural calcite were reacted in a piston-cylinder at 100°C intervals from 800°C–1200°C at ~23 kbar. Two starting calcite/grossularite mixtures were used, one with

an initially positive calcite-grossularite oxygen isotope fractionation and the other with an initially negative fractionation. Each run consisted of two ~25 mg charges encapsulated in platinum using each of the two starting materials. Capsules were encased in pyrex in a BaCO₃ pressure medium. After each experiment, the semi-sintered run products were recovered and isotopically analyzed. After grinding, charges were split into two subequal aliquots. The first of these was treated with ~1.4 M acetic acid for ~1 hour to eliminate any carbonate present, then analyzed with ClF₃ on the laser extraction line at Royal Holloway. The carbonate of the second aliquot was analyzed on an automated carousel using phosphoric acid at ~90°C and corrected for the temperature of extraction. All isotope analyses were done on a VG Prism and calibrated with NBS-19 and NBS-30 standards. SEM and XRD analyses of run products from the untreated aliquot verified that their major element compositions had not changed during reaction. Reaction times ranged from 3 days at the highest temperatures to 5 days at the lowest temperatures.

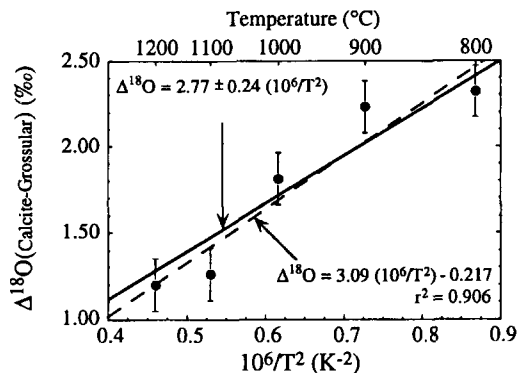


FIG. 1. Plot of experimentally determined equilibrium oxygen isotope fractionation between calcite and grossular as a function of inverse absolute temperature squared. Least-squares fits to the data both unconstrained (dash) and constrained (solid) to go through the origin are shown.

Results

The results of our experiments are summarized in a plot of $\Delta^{18}\text{O}(\text{calcite-grossular})$ fractionation as a function of the inverse square of the absolute temperature (Fig. 1). Error bars are estimates of the 2σ errors. According to theory (Urey, 1947), the intermineral fractionation should go to zero at infinite temperature. The equations for an unconstrained least squares fit to the data and a least squares fit constrained to go through the origin are both shown for comparison in Fig. 1. The former fit yields a small negative intercept and a slightly higher temperature coefficient than the latter fit.

The line through the origin yields a temperature coefficient for the calcite-grossular oxygen isotope fractionation of 2.77 ± 0.24 (2σ). This result has been combined with the compilation of

TABLE 1. Temperature coefficients, A, for inter-mineral oxygen isotope fractionations for the functional form $A \cdot 10^6/T^2$.*

	Cc	Ab	An	Di	Gr	Fo	Mt
Qtz	0.38	0.94	1.99	2.75	3.15	3.67	6.29
Cc		0.56	1.61	2.37	2.77	3.29	5.91
Ab			1.05	1.81	2.21	2.73	5.35
An				0.76	1.16	1.68	4.30
Di					0.40	0.92	3.54
Gr						0.52	3.14
Fo							2.62

*Bold data from this study; other data from Chiba *et al.* (1989).

Chiba *et al.* (1989) to generate a table of internally consistent temperature coefficients for inter-mineral fractionation factors based upon calcite-

mineral oxygen isotope exchange experiments (Table 1).

Our experimental data may be directly applicable to skarn terrains where grossular-rich garnets are found with calcite. While compositional effects have to be examined, the grossular data, combined with the data in Table 1 should be helpful in interpreting garnet-mineral oxygen isotope fractionations in natural settings, especially garnet-olivine and garnet-pyroxene fractionations in ultramafic rocks.

References

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