Oxygen isotope fractionation between zircon and water: experimental determination and comparison with quartz-zircon calibrations

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Abstract: Oxygen isotope fractionation between synthesised zircon and water has been experimentally quantified at 700, 800, 900, and 1000 °C. The results are interpolated by: $\Delta_{zrn\text{-}H2O} = -3.70 + 2.74 \pm 0.19 \ x^2$, where $x = 10^3/T$ (K). Combined with the fractionation between quartz and water (Bottinga & Javoy, 1973) this yields: $\Delta_{qtz\text{-}zm} = 1.36 \ x^2$.

Theoretical evaluations of the reduced partition function ratios for zircon and two (α- and β-) modifications of quartz are expressed in terms of the following polynomials:
$1000 \ \ln f_{zrn} = 8.3306 \ x^2 + 1.9402 \ x - 0.6896$ (400 < T < 1100 °C)
$1000 \ \ln f_{\alpha\text{-}qtz} = 7.8963 \ x^2 + 7.4091 \ x - 3.6015$ (200 °C < T < α-quartz stability field)
$1000 \ \ln f_{\beta\text{-}qtz} = 9.3362 \ x^2 + 2.4514 \ x - 0.7844$ (β-quartz stability field up to 1100 °C).

These expressions are in excellent agreement both with the experimentally derived factors of oxygen isotope fractionation for β-quartz and zircon, and the incremental calibrations for α-quartz and zircon (Hoffbauer *et al.*, 1994). The effect of α-β-quartz transition on oxygen isotope fractionation implies, that those calculations, anchored to the theoretically evaluated reduced partition function ratios of quartz (*e.g.*, Zheng, 1993), can predict fractionations only within the P-T stability field of the respective modification of quartz (*i.e.* α-quartz).

Key-words: oxygen isotopes, zircon water fractionation, quartz, geothermometry.

Introduction

Two main reasons have attracted interest in the oxygen isotope systematics of zircon since the development of new methods has overcome the previously dominating problems of analysing tiny amounts of refractory minerals. Firstly, low mobility of oxygen in zircon when compared to many other minerals (Watson & Cherniak, 1997) implies preservation of the "primary" isotopic compositions even if zircon has been subjected to a complex superimposed history. Secondly, rock forming minerals, which are commonly used for oxygen isotope measurements, typically contain low abundance of radiogenic elements. Hence, considerable problems arise when linking oxygen isotopic results (conditions of processes) with geochronology (ages of the processes). Zircon may serve as an ideal tool to relate geochronological and stable isotope data in one and the same phase, thereby allowing the U-Pb results to be interpreted in a petrological sense.

Equilibrium fractionation of oxygen isotopes between zircon and other phases must be known in order to interpret the measured oxygen isotope compositions in terms of geothermometry, equilibrium – disequilibrium processes and fluid – rock interactions. Zircon – mineral fractionations were quantified using several methods: crystal dynamic approach (Kieffer, 1982); the semi-empirical and theoretical methods of increments (Hoffbauer *et al.*, 1994; Zheng, 1993), the method of site potentials (Smyth, 1989), and natural distribution of isotopes in systems including zircon ("natural" calibration) (Valley *et al.*, 1994). The results of the crystal dynamic modelling by Kieffer (1982) were based on the available data on vibrational frequencies and a simplified evaluation of frequency shifts upon isotopic substitutions. Therefore, the results should be recalculated using modern estimates of the input parameters. Values of the site potentials (s.p.) vary substantially within a single mineral (Smyth, 1989), so that the deviations of oxygen isotope

partition functions from regressions using s.p. may be relatively high. The natural calibration by Valley *et al.* (1994) is based on a limited range of conditions and the assumption that garnet and zircon have similar closure temperatures for oxygen exchange.

The aim of the present work is to quantify oxygen isotope fractionation between zircon and water through laboratory experiments and to combine the data for use with other thermometers. Synthesis experiments were performed to obtain fractionation factors between zircon and water at high temperatures (700-1000 °C). The experimental data were then combined with quartz – water fractionations, and compared to the known mineral – mineral calibrations for oxygen isotope exchange, using quartz as a reference phase. Following a previously developed approach (Clayton & Kieffer, 1991, Chacko *et al.*, 1996), the theoretical calculation of fractionation between minerals was linked to the experimental data by adjusting the calculated partition function ratios of zircon.

Experimental methods

Zircons were synthesised at 2000 MPa pressure from reagent-grade ZrO_2 and SiO_2 using conventional hydrothermal techniques (Frondell & Collette, 1957; Caruba *et al.*, 1975). The charges consisted of approximately 80 mg mixture of solid reagents, weighed to give equimolar amounts of oxygen, and *ca.* 200 mg of doubly distilled water, sealed in 5 by 30 ± 6 mm platinum capsules. Temperature was stabilised at 700, 800, 900, and 1000 °C by an automatic high-precision (± 0.5 °C) potentiometer that was connected to a thermocouple close to the capsule. Five additional thermocouples were evenly placed along the reaction zone to monitor temperature gradients (± 15 °C). Run duration varied from 105 to 290 hours. After the completion of the experiment, ampoules were cooled to room temperature over about 30 minutes, weighed again to check for leakage and centrifuged before opening. No salts, which are commonly used to enhance rate of zircon synthesis (Frondell & Collette, 1957; Caruba *et al.*, 1975), were added to the reagents in order to avoid possible effects of dissolved ions on oxygen isotope fractionation (Truesdell, 1974).

Water and solid products were carefully separated and the solid phase was dried at 120 °C. X-ray diffraction and scanning electron microscope examinations showed no evidence of impurities in zircon.

Oxygen was extracted from zircon by reaction with ClF_3 (Borthwick & Harmon, 1982) at 550 to 650 °C and subsequently converted to CO_2 by the carbon reduction procedure. Analyses were made on a MI-1201V mass spectrometer with a dual inlet system. Standards (quartz GIN-1, 9.3 ‰) were analysed repeatedly during the period of this study and yielded reproducible results within ± 0.2 ‰ (1σ). Our analyses of NBS-28 give 9.65 ± 0.15 ‰ (1σ on the mean). The oxygen yields, measured on CO_2, were determined manometrically and are within the precision limits (± 2 %) of the expected values.

Water was converted to CO_2 for the isotopic analyses using guanidine hydrochloride $(NH_2)_2CNH*HCl$ (reagent

Table 1. Oxygen isotope composition ($\delta^{18}O$, SMOW) of synthetic zircon and H_2O.

$\delta^{18}O$			$1000\ln\alpha_{ij} \approx \delta^{18}O_i - \delta^{18}O_j$	
Zrn		H_2O [1]	Zrn – H_2O [1]	Qtz – Zrn [2]
Run 318/3; T = 700 °C, duration 290 hours				
-7.25±0.10(3)	-7.25	-6.46±0.11(5)	-0.79±0.15	1.42
Run 304/4; T = 800 °C, duration 120 hours				
-6.80±0.15(5)				
-6.76±0.04(4)	-6.88±0.10(1)	-5.57±0.02(2)	-1.31±0.10	1.17
-7.08±0.13(5)				
Run 306/1; T = 900 °C, duration 120 hours				
-6.50±0.08(3)	-6.41±0.09(1)	-4.64±0.17(5)	-1.77±0.19	1.05
-6.32±0.13(3)				
Run 306/4; T = 900 °C, duration 110 hours				
-6.33±0.03(4)	-6.33	-4.48±0.18(5)	-1.85±0.18	1.13
Run 314/2; T = 1000 °C, duration 105 hours				
-5.94±0.07(4)	-5.94	-3.92±0.10(3)	-2.02±0.12	0.85
Run 314/3; T = 1000 °C, duration 105 hours				
-6.34±0.26(3)				
-6.21±0.25(4)	-6.18±0.09(1)	-4.25±0.11(3)	-1.93±0.14	0.75
-6.24±0.14(4)				
-5.91±0.20(4)				

Comments: [1] average on the splits of one experiment ± 1σ (standard error on the mean), number in brackets refer to number of separate splits;
[2] $1000 \ln \alpha_{qtz-H2O} \approx -3.7 + 4.1 \times 10^6/T^2 - 1000 \ln \alpha_{zrn-H2O}$, (T in K) (Bottinga & Javoy, 1973).

quality) (details described by Boyer *et al.*, 1961: see their Modification 4). The standard deviations of the calculated means for each run are listed in Table 1. Precision of the single water analyses was about ± 0.25 ‰ (1σ).

Notation

Oxygen isotope ratios are expressed in terms of the conventional $\delta^{18}O$ values (‰) relative to V-SMOW (an abbreviation "δ" instead of $\delta^{18}O$ is used throughout the paper). Fractionation of oxygen isotopes between two phases, i and j, is quantified by $1000 \ln\alpha_{ij} = \delta_i - \delta_j$.

Results

The analytical data for zircons (zrn) and water are given in Table 1 with the estimated fractionations. A least square error-weighted fitting to the results (Williamson, 1968) using the two-term polynomial $1000 \ln\alpha \approx a + bx^2$, where $x = 10^3/T$ (K), (Bottinga & Javoy, 1973) yields:

$$1000 \ln\alpha_{zrn-H2O} = -3.71 \pm 0.14 + 2.75 \pm 0.18\, x^2 \quad (R^2 = 0.98) \quad (1)$$

The value obtained for "*a*" in (1) is fairly close to the expected value of −3.7 for high-temperature fractionations between anhydrous silicates and water (Bottinga & Javoy,

1973). Constraining the term "*a*" to a value of –3.7 for the experimental results leads to the following interpolation:

$$1000 \ln\alpha_{zrn-H2O} = -3.70 + 2.74 \pm 0.19 \, x^2 \, (R^2 = 0.97) \qquad (2)$$

Our results apparently disagree with the incremental calibrations of Zheng (1993). For example, the incremental calculations of the oxygen isotope fractionations at 800, 900, and 1000 °C give –3.42, –3.23, and –3.04 ‰, respectively, which are considerably (2.1 to 1.2 ‰) below the present experimental results (Table 1).

In order to incorporate the experimental results into available sets of oxygen isotope geothermometers, mineral – pair fractionations should be used rather than mineral – water fractionations (Matthews *et al.*, 1983). This requires a combination of the zrn-H$_2$O data with some known and reliable calibration of oxygen isotope fractionation factors as a function of temperature between another mineral and H$_2$O. It is convenient to use quartz (qtz) as a reference phase, although several calibrations for qtz-water oxygen isotope fractionation are known that disagree with each other. In this work, the expression $1000 \ln\alpha_{qtz-H2O} = -3.7 + 4.10 \, x^2$ (Bottinga & Javoy, 1973) is used because (i) it is also based on experimental data obtained at high temperatures; (ii) at more than 700 °C it agrees well with the theoretical calibration of Shiro & Sakai (1972); (iii) in the resulting expression for qtz-zrn fractionation ($1000 \ln\alpha_{qtz-zrn} = 1.36 \, x^2$) the term "a" is cancelled which satisfies the high-temperature approximation for isotopic fractionation (Bottinga & Javoy, 1973). Qtz-water oxygen isotope fractionations calibrated experimentally by Clayton *et al.* (1972) and Matsuhisa *et al.* (1979) are valid below 800 °C and extrapolations to higher temperatures may not be justified.

The estimated fractionations between qtz and zrn are lower (at any given temperature) than those predicted from any known theoretical (Kieffer, 1982, a line K in Fig. 1), empirical (Valley *et al.*, 1994), or semi-empirical calibrations (lines H and Z, Fig. 1). The differences between the results of this study and the other calibrations vary from 0.4 to 0.6 ‰ (compared to those deduced by the increment method of Hoffbauer *et al.*, 1994) up to 1.2 to 1.8 ‰ (compared to the modified incremental method of Zheng, 1993). The theoretical evaluations by Kieffer (1982) also yield results, which are 1.1 to 1.6 ‰ higher.

Discussion

Principal errors of experimental calibrations may be related to the kinetics of isotope exchange reactions and a difficulty of attaining and preserving equilibrium during experiments. During the syntheses of zircon the initial crystals formed while the system is heating up, may have been shielded from subsequent oxygen isotope exchange by new crystal growth (*e.g.*, O'Neil, 1986). Thus, the new layers of crystallising substance may retain isotope ratios that were established at temperatures less than that registered for an experiment. This effect is pronounced below 550 °C (Clayton *et al.*, 1972) because at higher temperatures the rate of diffusion is relatively high for most minerals. However, for zircon the effect of isolation of early-formed crystals cannot be ruled
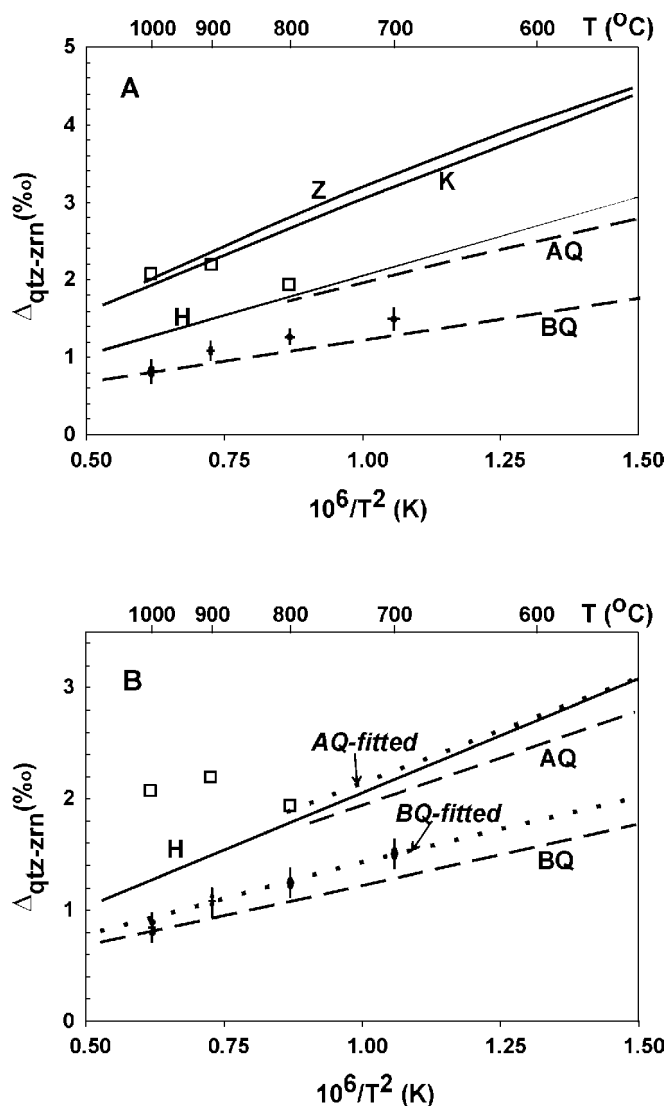

Fig. 1. Oxygen isotope fractionations between quartz and zircon: H (Hoffbauer *et al.*, 1994), Z (Zheng, 1993), K (Kieffer, 1982), open squares (Matsuhisa *et al.*, 1979). AQ, BQ (dashed lines) – calculated between α-quartz and zircon and β-quartz and zircon, respectively. AQ- and BQ-fitted (dotted lines) – reduced partition function ratios for zircon calculated to fit the experimental data points. The experimentally derived data points are combined with qtz-water calibrations of Bottinga & Javoy (1973) (open circles with ± 2σ error bars).

out even at higher temperatures due to slow oxygen diffusion in zircon (Watson & Cherniak, 1997). The discrepancy between our quartz – zircon fractionations and other calibrations illustrated in Fig. 1 is not considered to be related to such analytical problems as there is no systematic tendency of our calibration to approach the other calibrations with increasing temperature, which would be expected if oxygen diffusion increases in zircon with increasing temperature. Furthermore, the 100 % oxygen yields for zircon indicate that water, which may have been trapped in fluid inclusions and shifted the measured oxygen isotope ratios, did not occur in measurable amounts. These considerations cannot serve as a proof, but suggest critical analysis of the known

qtz-zrn oxygen isotope fractionation factors deduced by other methods.

Among the known calibrations, the most advanced and reliable method is based on the crystal dynamic properties and uses statistical mechanical calculations of the reduced partition function ratios (f) for isotopic substances (Kieffer, 1982). The equilibrium fractionation factors between minerals i and j can then be obtained by subtraction: $1000 \ln\alpha_{ij} = 1000 \ln f_i - 1000 \ln f_j$. Unfortunately, the calculations (Kieffer, 1982) were made only for the low-temperature modification of quartz (α), which is stable below 573 °C (at 1 bar). Estimations of the effect of α-β transition on oxygen isotope fractionation yield 0.8 ‰ (Shiro & Sakai, 1972) and 1.5 ‰ (Kawabe, 1978) and, therefore, this effect cannot be neglected at least in the theoretical calculations.

Our evaluations of the reduced partition function ratios using the appropriate sets of the input parameters (Alekhina *et al.*, 1973; Kawabe, 1978) (lines AQ and BQ in Fig. 1) can be interpolated by the following polynomials:

$1000 \ln f_{zrn} = 8.5107x^2 + 1.9625\ x - 0.6977\ (400 < T < 1100\ °C)$
$1000 \ln f_{\alpha\text{-qtz}} = 7.8963x^2 + 7.4091\ x - 3.6015\ (200\ °C < T < \alpha$-quartz stability field)
$1000 \ln f_{\beta\text{-qtz}} = 9.3362x^2 + 2.4514\ x - 0.7844\ (\beta$-quartz stability field up to 1100 °C)

Calculated fractionation factors between α-quartz and zircon are fairly close to those predicted by the method of increments (Hoffbauer *et al.*, 1994) (Fig. 1a, b). Our calculations also yield consistent results, if combined with the experimental data on α-quartz – water fractionation (Matsuhisa *et al.*, 1979) at 800 °C (Fig. 1b). However, the results of Matsuhisa *et al.* (1979) extrapolated to 900 and 1000 °C and combined with the experimental data of the present work would predict qtz-zrn oxygen isotope fractionation, which is close to the results of Zheng (1993) (Fig. 1a, open squares). This apparent coincidence has no meaning because qtz-H_2O oxygen isotope fractionation, which is an independent base for calculation of increments by Zheng (1993), differs substantially from the results of Matsuhisa *et al.* (1979).

The calculated fractionation factors between β-quartz and zircon are not far from the experimentally derived data (Fig. 1a). Thus, the discrepancy between the curves, deduced from the experimental results and the incremental results, are mainly caused by the stability of the β-quartz in the temperature range of the experiments.

The calculated partition function ratios are further adjusted to optimise the fit of β-quartz – zircon fractionation to the experimental data (in the sense of Clayton & Kieffer, 1991; Chacko *et al.*, 1996) by modifying frequency shifts upon the oxygen isotopic substitution in zircon (Fig. 1b). The improved reduced partition ratio of zircon is:

$1000 \ln f_{zrn} = 8.3306\ x^2 + 1.9402\ x - 0.6896\ (400 < T < 1100\ °C)$

It is noteworthy that after the adjustment the calculated fractionation between another quartz modification (α) and zircon (AQ-fitted, Fig. 1b) practically coincides with the results of Hoffbauer *et al.* (1994) (H, Fig. 1b). This coinci-

dence appears to be a good justification both for the reliability of the experiments and the calculated fractionations. As was stated before for other minerals (Clayton & Kieffer, 1991, Chacko *et al.*, 1996), the theoretical models developed for zircon and the two quartz modifications provide reliable guidelines for extrapolating the fractionation data outside the experimentally investigated temperature range and the combined experimental / theoretical approach takes advantage of the best features of each technique. The obtained results additionally demonstrate that those semi-empirical calculations, anchored to the **theoretically** evaluated reduced partition function ratios of quartz (*e.g.*, Zheng, 1993), can predict fractionations only within the P-T stability field of the respective modification of quartz (*i.e.* α-quartz).

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