Slow oxygen diffusion rates in igneous zircons from metamorphic rocks

William H. Peck,[1,*] John W. Valley,[2] and Colin M. Graham

[1]Department of Geology, Colgate University, Hamilton, New York 13346, U.S.A.
[2]Department of Geology and Geophysics, University of Wisconsin, Madison, Wisconsin 53706, U.S.A.
[3]Department of Geology and Geophysics, University of Edinburgh, Edinburgh EH9 3JW U.K.

ABSTRACT

Empirical tests of oxygen exchange rate in zircon crystals from amphibolite- and granulite-facies metamorphic rocks of the Grenville Province demonstrate preservation of igneous $\delta^{18}O$ through protracted igneous and metamorphic histories, forming the basis of quantitative estimates of diffusion rate. Granitic orthogneisses, which cooled slowly after granulite-facies metamorphism, show no consistent relationship between zircon size and $\delta^{18}O$, indicating slow oxygen diffusion. Detrital zircon crystals from granulite-facies quartzites are out of equilibrium with their host rocks, and no consistent correlation is seen between $\delta^{18}O$ and grain size in high-precision analyses by laser fluorination of multiple grains, sieved for size. In a single sample, individual detrital zircon crystals preserve grain-to-grain variability in $\delta^{18}O$ (determined by ion microprobe), ranging from 5.0 to 9.5‰. The inherited cores of some zircon crystals are up to 5.6‰ lower than igneous overgrowths, showing that gradients of 5.6‰ can be preserved over 50 μm even at magmatic conditions. All of these lines of evidence show that oxygen diffusion in zircon in these rocks was slow both during metamorphism and during slow cooling of 1–3 °/m.y. Calculations based on the measurements indicate that the oxygen diffusion rate in zircon (D) must be $\geq 10^{-22}$ cm²/s at 600 °C to explain $\delta^{18}O$(zircon) values measured from Grenville quartzite and orthogneiss. This value is consistent with the experimentally determined value of $D = 2 \times 10^{-27}$ cm²/s for dry diffusion experiments extrapolated to 600 °C (Watson and Cherniak 1997). These results indicate that oxygen-isotope analysis of zircon may be used to see through granulite-facies metamorphism and anatexis, and to unravel crustal recycling processes in igneous rocks.

INTRODUCTION

Knowledge of the oxygen diffusion rate in minerals is essential for the use of oxygen-isotope systematics in igneous and metamorphic rocks to answer questions of peak temperature, cooling rate, and petrogenesis. The experimental database of oxygen diffusion in rock-forming minerals is substantial (e.g., Brady 1995; Cole and Chakraborty 2001), but relatively few studies have focused on empirically constraining oxygen diffusion rates (but see Sharp 1991; Valley and Graham 1991; Sharp and Jenkin 1994; Edwards and Valley 1998). Experimental diffusion rates are commonly used as input parameters in numerical models of stable-isotope fractionations in rocks, usually with regard to isotopic resetting during cooling (Giletti 1986; Farver 1989; Eiler et al. 1992,1993; Farquhar et al. 1993; Kohn 1999). In this study, we present new data constraining the oxygen diffusion rate in zircon crystals from orthogneiss and quartzite.

Many oxygen diffusion experiments have shown that the presence of H_2O (i.e., hydrothermal experiments with $P_{H_2O} \approx 1$ kbar) speeds oxygen diffusion relative to anhydrous experiments (see Elphick and Graham 1988; Graham and Elphick 1991; Cole and Chakraborty 2001). The difference in diffusion rates for the same mineral between these "wet" and "dry" experiments is very large when extrapolated to lower tempera-

tures, resulting in closure temperatures (Dodson 1973) that differ by hundreds of degrees. For zircon at 600 °C, the difference in D is indicated to be seven orders of magnitude (Watson and Cherniak 1997).

The purpose of this study is to place empirical limits on the rate of oxygen diffusion in natural zircon crystals, in order to determine if zircon should preserve primary $\delta^{18}O$ values through subsequent thermal events. We compare our results to hydrothermal and dry experiments for oxygen diffusion in zircon (Watson and Cherniak 1997). Hydrothermal experiments at P_{H_2O} = 0.07–10 kbar yield fast diffusion rates (Fig. 1), suggesting closure temperatures to oxygen diffusion on the order of 500 to 550 °C for average zircon radii and slow cooling (1 to 5 °C/m.y.). Dry experiments have much slower diffusion rates, yielding closure temperatures >900 °C for average zircon radii and slow cooling (Watson and Cherniak 1997). Under hydrous conditions, fast diffusivities overwhelm the mechanisms that dominate the "dry" experiments (attributed to migration of oxygen interstitials; Crocombette 1999).

Crystalline, non-metamict zircon has been shown to be retentive of igneous oxygen-isotope ratios, even after protracted metamorphic (Valley et al. 1994; Peck et al. 2001), igneous (King et al. 1998; Valley et al. 1998b; Bindeman and Valley 2001), and hydrothermal histories (Gilliam and Valley 1997; King et al. 1997; Monani and Valley 2001; see Valley 2003). Calculations based on hydrothermal experiments (Watson and Cherniak 1997) predict that many of the zircons in the above

studies should have exchanged completely with their host rocks, thus resetting $\delta^{18}O$(zircon). To understand this apparent discrepancy, and to constrain diffusion coefficients for zircon in nature, we examine the oxygen-isotope systematics of amphibolite- and granulite-facies lithologies that have cooled slowly after metamorphism. We use both high-precision laser fluorination of zircon separates and in situ ion-microprobe analysis to assess oxygen-isotope heterogeneity and zoning to constrain oxygen diffusion rates.

ANALYTICAL TECHNIQUES

Samples weighing 10 to 40 kg were crushed, and zircon crystals were separated using a shaking table, heavy liquids, and magnetic techniques. Polished grain mounts of zircon were imaged with back-scattered electrons (BSE) and cathodoluminenence (CL) using an SX-50 electron microprobe. Zircon splits were separated based on magnetism, hand-picked for purity, and soaked in cold HF to identify and dissolve metamict crystals. This screening was to identify samples that are obviously altered and may have experienced non-diffusional oxygen exchange. Note that if altered samples (e.g., metamict zircon with dampened CL) were analyzed inadvertently, it would cause the oxygen diffusion rate to be overestimated, and not change the conclusions of this study.

Minerals were analyzed for $\delta^{18}O$ by laser fluorination at the University of Wisconsin; data are given in Tables 1 and 2. This method analyzes 1–3 mg samples with high precision and accuracy (typically better than ±0.1‰). Oxygen was liberated from mineral separates by heating with a CO_2 laser in the presence of BrF_5 (see Valley et al. 1995). Forty-four aliquots of garnet standard (UWG-2) were measured on the 11 days of analysis. The overall raw $\delta^{18}O$ of UWG-2 averaged 5.71 ± 0.12‰ (1 standard deviation reported, 1 s.e. uncertainty in the mean = 0.02). This is within the error of the long-term laboratory

average for UWG-2 of 5.74 ± 0.15‰ ($n = 1081$, 1 s.e. = 0.005‰ ; Valley et al. 1995). The daily mean value of UWG-2 also averaged 5.71‰, and daily precision (1 s.d.) averaged 0.08 ± 0.03‰. Forty-eight zircon samples were analyzed in duplicate, and reproducibility averaged 0.07 ± 0.06‰. Some zircon splits were ground to a powder in a boron carbide mortar and pestle, which makes reaction while heating with the CO_2 laser more reproducible (use of a powder reduces samples jumping from the holder). Zircon splits that have been analyzed both as powders and whole grains have identical average $\delta^{18}O$ values, but grinding often improved reproducibility from ca. ±0.08‰ to ±0.06‰ (Peck 2000). Analyses were corrected to the VSMOW scale by the amount that daily UWG-2 values deviated from 5.80‰, its accepted value (Valley et al. 1995). This correction averaged 0.10‰ and was always less than 0.28‰.

Oxygen-isotope ratios for single grains of zircon from quartzites 97ADK2 and 97ADK4 were measured by ion-microprobe/secondary ion mass spectrometry (SIMS) on a modified Cameca ims 4f ion microprobe at the University of Edinburgh (see Valley et al. 1998a). Precision and accuracy are ±1.0‰ (1 s.d.) for this method, based on counting statistics and duplicate analyses. Gold-coated samples were sputtered with a $^{133}Cs^+$ beam defocused to a ~20 μm diameter spot. The resulting craters were ~3 μm deep. Secondary $^{18}O^-$ and $^{16}O^-$ ions were extracted with an energy offset of 350 ± 20eV. Sample analyses were standardized by bracketing analyses of a standard zircon of similar HfO_2 content, KIM-5 (Peck et al. 2001). 160 analyses of KIM-5 were made in the course of 192 sample analyses. Operating conditions, standardization, and data reduction are described in Peck et al. (2001) and raw data are given in Peck (2000). Table 3 summarizes ion-microprobe data.

Core and rim analyses were made on some individual grains. Single zircon crystals mounted in superglue (cyanoacrylate) were ground and polished through the center of each crystal longitudinally parallel to the *c*-axis, and the interior was analyzed for oxygen-isotope ratio. Grains were then freed from grain-mounts with acetone, and pressed into indium with their crystal growth faces upward flush with the metal (see Fig. 2). This procedure allowed the outermost ~3 μm of the crystal (the depth of the ion sputtered pit) to be analyzed.

EMPIRICAL TESTS OF OXYGEN DIFFUSION IN ZIRCON

Two high-grade lithologies (orthogneiss and quartzite) were selected for empirical diffusion studies. In quartzite, non-metamict detrital zircon and host rock were out of oxygen-isotope equilibrium before high-grade metamorphism. The approach of these zircon crystals toward isotopic equilibrium with their host rocks during metamorphism is rate limited by oxygen diffusion through the zircon crystal structure. We also examined zircon crystals from various metaigneous rocks, to assess oxygen diffusion in rocks from which zircon would most typically be analyzed. In orthogneiss, non-metamict zircon is assumed to be in initial magmatic equilibrium with its host rock, but to experience diffusive exchange during metamorphism and subsequent cooling. If oxygen diffusion rates in zircon are fast
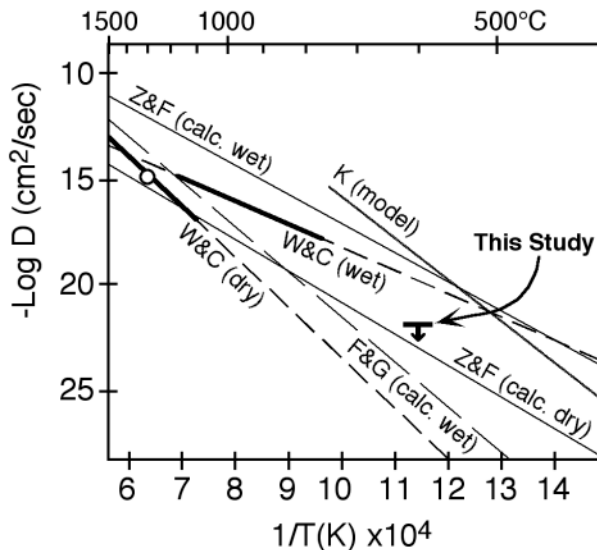

FIGURE 1. Arrhenius plot of experimentally determined and calculated oxygen diffusion rates in zircon. Hydrothermal "W&C (wet)" and anhydrous "W&C (dry)" experiments (Watson and Cherniak 1997). Dark line shows range of experimental temperatures, short dashes are extrapolation. "F&G (calc. wet)" (long dashes), "Z&F (calc. wet)", and "Z&F (calc. dry)" (fine lines) are calculated diffusion rates (Fortier and Gilletti 1989; Zheng and Fu 1998). "K model" refers to "fictive" diffusion coefficients calculated for a cooling metabasite (see text; Kohn 1999). The circle is the anhydrous datum of Muehlenbachs and Kushiro (1974). The arrow shows the empirical estimate from this study, $D < 10^{-22}$ cm²/s at 600 °C.
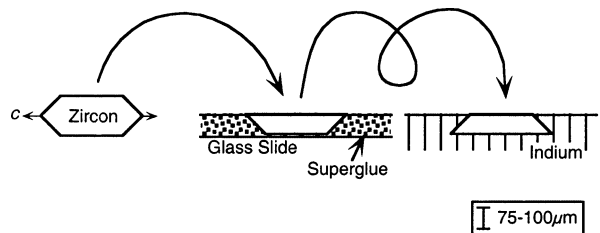

FIGURE 2. Cartoon of sample handling for single detrital zircons from Adirondack quartzites. Single grains were mounted in superglue and were ground through the center of each zircon longitudinally parallel to their *C*-axes. After ion-microprobe analysis, zircons were freed from grain mounts with acetone and were pressed into indium with their crystal growth faces upward and flush with the metal for additional ion microprobe analysis of the outermost 3 μm of the crystal.

TABLE 1. Oxygen isotope ratios of zircon from granulite facies orthogneiss (Adirondack Mountains, New York)

Sample	Peak Meta. Temp	Mag.	δ¹⁸O Zircon >149μm	δ¹⁸O Zircon 149–105μm	δ¹⁸O Zircon 105–74μm	δ¹⁸O Zircon 74–53μm	δ¹⁸O Zircon <53μm	δ¹⁸O Zircon Bulk
LDT tonalite gneiss	675 °C	M-1	7.29 ± 0.04	7.38 ± 0.04	7.48 ± 0.03	7.70 ± 0.10	7.84 ± 0.03	
TOE metagranite	675 °C	M0	8.33 ± 0.06	8.42 ± 0.03	8.25 ± 0.02	8.40 ± 0.05	8.28 ± 0.14	
AM86-8 charnockite	750 °C	M-2	8.19 ± 0.03	8.21 ± 0.07	8.24 ± 0.01	7.95 ± 0.11	8.30	
98LB3 metasyenite	675 °C	NM2	8.39 ± 0.08	8.11 ± 0.05	8.15	8.14 ± 0.00	8.27 ± 0.07	8.22 ± 0.01
AM86-6metagranite	725 °C	M-2	7.74 ± 0.13	7.66 ± 0.06 >149μm	7.70 ± 0.02 149–74μm	7.64 ± 0.02 <74μm	7.75 ± 0.10	
NOFO-1 metagranite	725 °C	M0	8.26 ± 0.04	8.35 ± 0.02	8.33 ± 0.00			

Notes: Analyses of δ¹⁸O are reported in standard per mil (‰) notation relative to VSMOW. Analysis is discussed in text. Mag. indicates magnetic (M) or non-magnetic (NM) and angle of side tilt on the Frantz magnetic separator. Analyses of different size zircons separated in bulk by sieving (e.g., 149–105 μm, indicating zircon diameters) are indicated. All samples were powdered with a boron carbide mortar and pestle before analysis. Duplicate analyses are indicated by ±, with the average reproducibility shown (half the difference between analyses). Peak metamorphic temperatures are after Bohlen et al. (1985). Sample locations are given in Peck (2000).

TABLE 2. Oxygen isotope ratios of zircon and other minerals from amphibolite and granulite facies Grenville quartzites (Ontario and New York)

Sample	Peak Meta. Temp.	Mag.	δ¹⁸O Zircon >149 μm	δ¹⁸O Zircon 149–105 μm	δ¹⁸O Zircon 105–74 μm	δ¹⁸O Zircon 74–53 μm	δ¹⁸O Zircon <53 μm	δ¹⁸O Quartz		δ¹⁸O Garnet	
92ADK7	725°C	NM2		9.10 ± 0.07p	9.35 ± 0.04p	9.68 ± 0.04p	10.14 ± 0.09p	14.75c	14.56c	12.48c	12.50c
								14.91c	14.59c		
								14.38c	14.68c		
97ADK2	675°C	NM2	9.00 ± 0.01	9.25 ± 0.01	9.51 ± 0.03	9.62 ± 0.08		13.38b	13.72b	11.44c	11.09c
								13.02c	13.82c	11.13c	11.32c
								13.59c	13.84c	11.24c	
97ADK3	675°C	NM2	7.46 ± 0.21	7.81 ± 0.22	7.45±0.11	7.83 ± 0.12		12.90b	12.54b		
								12.56c	12.72c		
								12.65c	12.54c		
97ADK4	675°C	NM2	8.85 ± 0.22	9.05 ± 0.09	9.04 ± 0.03	8.72 ± 0.08		12.29b	12.08b	10.42c	9.56c
								11.81c	12.14c	9.81c	9.77c
								12.08c	12.11c		
99SR1	775°C	NM2			12.00p			14.62c	14.48c		
97WE10	750°C	NM3		8.93 ±0.01	8.17 ± 0.16	8.98 ± 0.19		13.85b	13.45c		
								13.59c	13.57c		
								13.65c			
97BM2	750°C	NM2			9.28 ± 0.05	8.72 ± 0.13		15.83b	15.81b		
								15.94c	15.64c		
								15.52c	15.73c		
SL2	750°C		7.76 ± 0.03	7.38							
Data from Valley et al. 1994											
Rt81	Zircon <75 μm			9.15				16.71	16.20		
CT1	Zircon 149–105 μm			9.60 ± 0.24				15.68	15.61		
CT2	Zircon >105 μm			9.82 ± 0.13				16.12			
SL1	Zircon >149 μm			7.91 ± 0.17				14.40	14.67		
SL2	Zircon 149–105 μm			7.90				14.14	14.21		

Notes: Analyses of δ¹⁸O are reported in standard per mil (‰) notation relative to VSMOW. Analysis is discussed in text. Mag. indicates magnetic (M) or non-magnetic (NM) and angle of side tilt on the Frantz magnetic separator. Analyses of different size zircons separated in bulk by sieving (e.g., 149–105 μm, indicating zircon diameters) are indicated. 'p' indicates samples which were powdered with a boron carbide mortar and pestle before analysis. Duplicate analyses are indicated by ±, with the average reproducibility shown (half the difference between analyses). For quartz and garnet 'b' indicates a bulk mineral separate and 'c' indicates a single mineral fragment. Peak metamorphic temperatures are after Anovitz and Essene (1990) and Bohlen et al. (1985). Sample locations are given in Peck (2000).

enough, zircon crystals of different sizes (separated by sieving) should show variable amounts of resetting reflecting the different closure temperatures of different crystal sizes.

GRENVILLE QUARTZITES

Quartzite samples were collected from granulite-facies localities in the Frontenac terrane (Ontario) and Adirondack Highlands (New York), and supplement the analyses of Frontenac terrane quartzites presented by Valley et al. (1994). Five samples were collected from the metasedimentary sequence in the Adirondack Highlands (ADK and SR sample numbers, Fig. 3). Samples 97ADK-2, 97ADK-3, and 97ADK-4 are from the southern Adirondack Highlands, and belong to the "Irving Pond Formation" as described by Wiener et al. (1984). Sample

92ADK7 was collected from the Swede Pond Quartzite (Eastern Adirondacks). Sample 99SR1 is an interlayered quartzite and calc-silicate lithology from the peak of Mount Pisgah (Central Adirondacks). This metasedimentary sequence is older than ~1.3 Ga (see Fig. 4; McLelland et al. 1988). In the Frontenac terrane, sample 97BM2 was collected from locality SL-1 of Sager-Kinsman and Parrish (1993). This sample contains striking heavy mineral layers that define relict cross-bedding. Sample 97WE10 was collected from locality CT-2 of Sager-Kinsman and Parrish (1993), and is a more typical massive quartzite. Most detrital zircon crystals in Frontenac terrane quartzites range from 1493 to 2580 Ma (37 single grain U-Pb ages), with two outliers yielding 1306 ± 16 Ma and 3185 ± 3 Ma (Sager-Kinsman and Parrish 1993). All but one quartz-
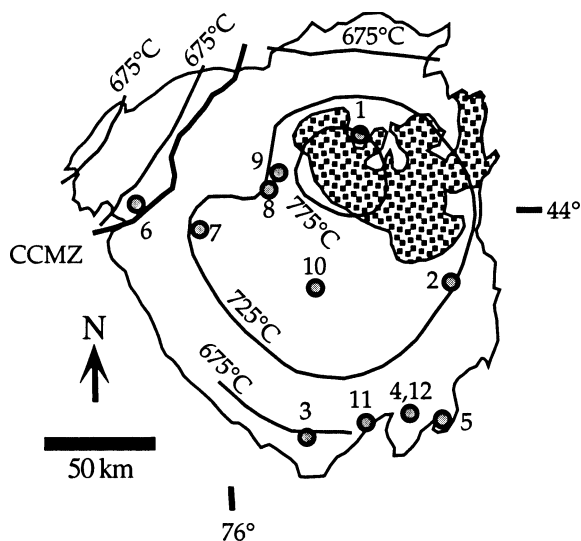
FIGURE 3. Sample location map for quartzite and orthogneiss samples from the Adirondack Mountains, New York. The area of Precambrian outcrop is shown. Isotherms for regional metamorphism are from Bohlen et al. (1985) and Kitchen and Valley (1995). Quartzites: 1 = 99SR1, 2 = 92ADK7, 3 = 97ADK2, 4 = 97ADK3, 5 = 97ADK4; Orthogneiss: 6 = 98LB3, 7 = NOFO-1, 8 = AM86-6, 9 = AC85-6, 10 = AM86-8, 11 = TOE, 12 = LDT. CCMZ = Carthage-Colton Mylonite Zone, stippled pattern is Marcy anorthosite massif.

TABLE 3. Summary of ion microprobe analyses of $\delta^{18}O$ in detrital zircon grains from Grenville quartzites 97ADK2 and 97ADK4

Crystal	$\delta^{18}O$ Grain Interior	n	$\delta^{18}O$ Inherited Core	n	$\delta^{18}O$ Crystal Face	n	Δ (CF–GI)
97ADK2							
1	6.6 ± 0.9	3			12.6 ± 0.5	3	6.1
2	5.9 ± 1.0	4					
3	6.5 ± 0.0	2			11.3 ± 1.0	2	4.8
4	7.9 ± 0.0	2					
5	8.0	1					
6	5.7 ± 0.4	9			12.8 ± 0.5	6	7.2
7	7.5 ± 1.1	4			11.4 ± 0.9	4	4.0
8	7.8 ± 0.5	3			9.3 ± 0.7	3	1.5
9	8.1 ± 0.4	4			11.8 ± 1.1	3	3.7
10	7.4 ± 0.4	4			10.9 ± 0.3	2	3.5
11	5.1 ± 0.4	4			9.8 ± 0.7	7	4.6
12	4.9 ± 0.5	4			11.3 ± 0.8	4	6.4
13	9.7 ± 0.4	4					
14	5.5 ± 0.6	5					
15	9.0 ± 0.5	7			12.7 ± 0.5	4	3.8
16	5.5 ± 0.4	4					
17	6.3 ± 0.6	4			10.5 ± 0.5	4	4.2
18	6.1 ± 1.0	4			11.1 ± 0.6	6	5.0
					Average = 11.28 ± 0.24	48	
97ADK4							
1	9.4 ± 0.7	4	8.6 ± 1.2	2	10.7 ± 0.4	2	1.3
2	10.0 ± 0.1	3	7.1 ± 0.0	2	10.0 ± 0.5	4	0.0
3	9.7 ± 0.5	5			9.8 ± 0.5	3	0.1
4	11.2 ± 1.0	3					
5	8.8 ± 0.7	4			10.1 ± 0.3	4	1.4
6	8.4 ± 1.3	3	6.5 ± 0.3	3	10.5 ± 0.3	4	2.1
7	11.3 ± 0.9	3			10.0 ± 2.0	2	−1.3
8	9.6 ± 0.6	9			10.0 ± 0.1	4	0.4
9	10.7 ± 0.5	3	5.1 ± 0.3	3	10.5 ± 0.9	4	−0.2
10	10.3 ± 1.1	3					
11	9.8 ± 0.5	4			11.7 ± 1.0	2	1.9
					Average = 10.30 ± 0.20	29	

Notes: Analyses are reported in standard per mil (‰) notation relative to VSMOW. Full ion probe data and data reduction are detailed in Peck (2000). One sigma uncertainty in the mean of each oxygen isotope ratio (±) is shown, n = number of spot analyses. Δ(CF-GI) shows the fractionation between crystal faces and grain interiors, which is large and variable in 97ADK2 and small in 97ADK4.

ite sample contains over 90% quartz, with minor to trace amounts of feldspars, micas, amphibole, pyroxene, garnet, oxides, and zircon. Sample 99SR1 is layered and contains abundant diopside and calcite in subequal proportions to quartz.

ANALYSIS OF $\delta^{18}O$(ZIRCON) BY LASER FLUORINATION

Different size splits of zircon (avg. radius ~20–90 μm) and quartz were analyzed from all quartzite samples, and garnet was analyzed from three samples (Table 2, Figs. 4 and 5). Zircon crystals from each quartzite sample are from a mixed population. Morphology and color are heterogeneous within each sample, and grains show variable amounts of rounding and abrasion. Note that these features are distinct from the broken grains often observed after separation of zircon crystals from igneous lithologies. We interpret the majority of zircon grains in quartzite to be detrital and from a mixture of sources, as is also illustrated by the range in ages in Frontenac zircons. The $\delta^{18}O$ zircon from "pure" quartzites (>90% quartz) ranges from 7.4 to 9.6‰, and the average $\delta^{18}O$ of quartz ranges from 12.1 to 15.7‰. There is a small variation in $\delta^{18}O$(quartz) observed in some samples when single pieces of quartz were analyzed (0.2 to 0.8‰, Table 2). This variability at the scale of 20 to 50 cm is expected given the large sample sizes crushed for analysis.

In the three garnet-bearing quartzites, constant quartz-garnet fractionations [Δ(Qtz-Gt) = 2.2–2.3‰] are observed. Because Δ(Zrc-Gt)~0 at high temperatures (Valley et al. 1994, 2003), similar, systematic fractionations should be seen between quartz and zircon if they equilibrated during metamorphism. The results in Figure 5 are consistent with equilibrium between quartz and metamorphic garnet, but show a distinct lack of

equilibration between quartz and detrital zircon. Only in 99SR1 [$\delta^{18}O$(zircon) = 12.00‰] is the fractionation between zircon and quartz consistent with metamorphic exchange, but this is likely to be a coincidence, as none of the other Adirondack samples have similar quartz-zircon fractionations. Values of $\delta^{18}O$(quartz) have a great deal of variability from sample-to-sample in quartzite, probably because of mixing of different sedimentary and diagenetic sources of quartz. In contrast, values of $\delta^{18}O$(zircon) are more constrained, similar to $\delta^{18}O$ values in igneous rocks (Peck et al. 2000, 2001; Valley 2003), and do not depend systematically on grain size (Fig. 6).

ANALYSIS OF $\delta^{18}O$(ZIRCON) OF INDIVIDUAL CRYSTALS BY ION MICROPROBE

Ion-microprobe analysis was undertaken in two quartzite samples to test for grain-to-grain oxygen-isotope variability among individual zircon crystals, and to test for diffusion profiles within single grains. Single zircon crystals (radius ≈88 μm) were hand-picked from the largest size split (Table 1). In-situ ion-microprobe analysis of $\delta^{18}O$ confirms the lack of equilibration during metamorphism. Variability is observed between the average $\delta^{18}O$ values of the interiors of zircon grains from 97ADK2,
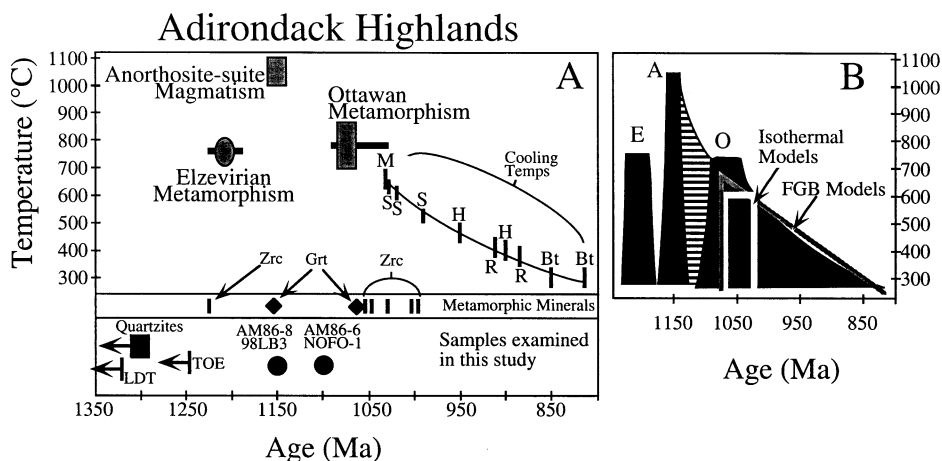
FIGURE 4. (A) Summary of temperature-time evolution of the Adirondack Highlands, after Bohlen et al. (1985); Mezger et al. (1991); Chiarenzelli and McLelland (1993); McLelland et al. (1996); Spear and Markussen (1997); and McLelland et al. (2001). Estimates of peak temperature of metamorphic events are shown, and durations of orogenic deformation are given as horizontal bars. Note that temperatures are well constrained for the Ottawan, but only generally known for the Elzevirian orogeny. Ages of minerals that formed above their closure temperatures (Tc) are plotted vs. T. M = Monazite, S = Sphene, H = Hornblende, R = Rutile; B = Biotite. Minerals that formed below their individual Tcs (metamorphic zircon and garnet) are not plotted against temperature, but likely formed ca. 600–700 °C (see McLelland et al. 2001). See text for geochronology of Adirondack Highlands samples (minimum ages shown by arrows). All Adirondack Highlands samples examined in this study experienced granulite-facies metamorphism during the Ottawan orogeny followed by slow cooling. (B) Summary of 4A showing the integrated thermal history of the Adirondack Highlands. Note that the thermal pulse of 1150 Ma anorthosite-suite magmatism may lead into Ottawan heating (shown by striped pattern), or temperature may drop to low values before rising again during orogeny. The thermal paths of modeling approaches are shown [Fast Grain Boundary (FGB) cooling and isothermal models], and are conservative relative to the integrated thermal history of the rocks modeled.

ranging from 5.0 to ~9.5‰ (Table 3, Fig. 7). This range is consistent with derivation from igneous rocks. It is interesting to note that the lowest observed $\delta^{18}O$ is ~5‰, a value in equilibrium with the mantle and consistent with derivation from a juvenile magma. For example, zircons from juvenile plutonic rocks of the 2.7–3.0 Ga Superior Province have $\delta^{18}O$ = 5.6 ± 0.5‰ (King et al. 1998), whereas high $\delta^{18}O$(zircon) (>7‰) is consistent with derivation from magmas with some supracrustal component (e.g., Peck et al. 2000, Valley 2003). Metamorphic zircon grown in high $\delta^{18}O$ metasedimentary rocks (e.g., ≥9‰) would also have high $\delta^{18}O$ values.

Comparison of interior and rim $\delta^{18}O$(zircon) values

In-situ analyses of the outer 3 mm of crystal faces of zircon crystals in 97ADK2 gave consistently higher $\delta^{18}O$ values than grain interiors (Fig. 7, Table 3). The average of all spot analyses of crystal faces in this sample is 11.3 ± 1.7‰ (n = 48 spots; 1 s.e. = 0.2‰). This result is consistent with oxygen diffusion profiles across the outermost few micrometers of the crystal. The $\delta^{18}O$ values of the crystal faces are the same (within uncertainty) as $\delta^{18}O$(garnet) from the same rock [average $\delta^{18}O$(garnet) = 11.24 ± 0.14‰, n = 5, 1 s.e. = 0.06‰], indicative of approach to oxygen-isotope equilibrium between zircon faces, garnet, and quartz during metamorphism.

We interpret the crystal face value of $\delta^{18}O$ as the result of diffusion into the igneous growth face and not growth of new zircon during metamorphism of the quartzite. Detrital rounding and abrasions are observed on most grains, and no metamorphic rims are visible by BSE or CL. To further evaluate the
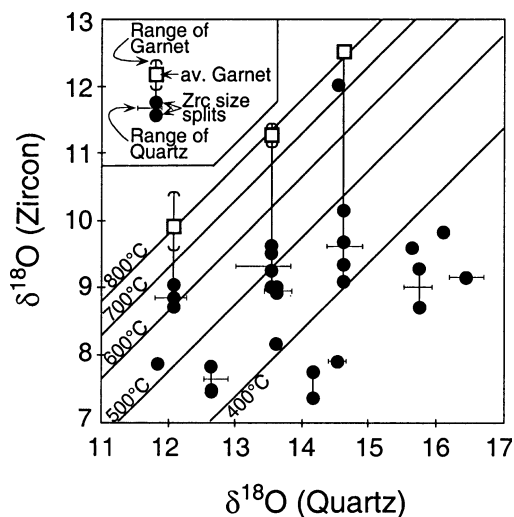

FIGURE 5. Values of $\delta^{18}O$(quartz) versus $\delta^{18}O$(detrital zircon) from Grenville quartzites. Data are from Table 2 and Valley et al. (1994). Analyses of zircons of different sizes (Fig. 6) from the same sample are connected by a vertical line, and garnet analyses (boxes) are indicated. Isopleths of temperature are the equilibrium $\Delta^{18}O$(Qtz-Zrc)· $\Delta^{18}O$(Qtz-Grt) (Valley et al. 1994, 2003). Values of $\delta^{18}O$(zircon) are clearly not in equilibrium with host quartz for the peak of metamorphism at 675 to 775 °C. In contrast, metamorphic garnet consistently shows high-temperature metamorphic fractionations (see Table 2).
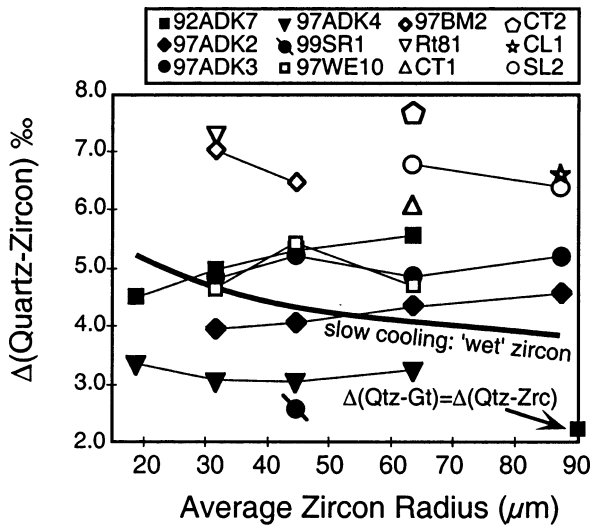
FIGURE 6. Oxygen-isotope fractionations between quartz and detrital zircons as a function of zircon size from Grenville quartzites. Shown also are predictions from Fast Grain Boundary (FGB) modeling of diffusive oxygen exchange during slow cooling using the "wet" diffusion rates of Watson and Cherniak (1997). Measured (metamorphic) garnet-quartz fractionations are shown with a filled square. The lack of systematic correlations between Δ(Qtz-Zrc) and zircon size indicates that oxygen diffusion in zircon is slower in natural samples than predicted by hydrothermal experiments.
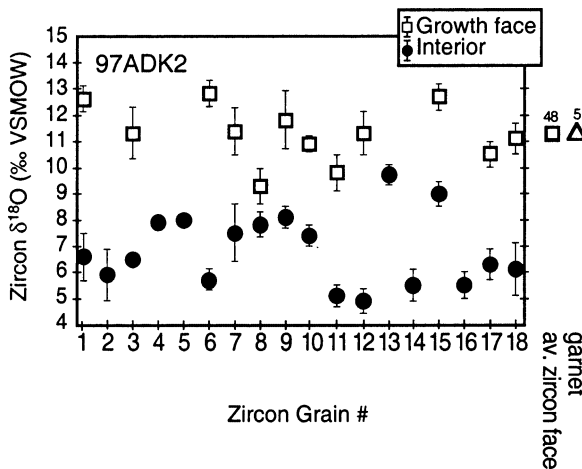
FIGURE 7. Ion-microprobe analyses of $\delta^{18}O$ in 18 individual detrital zircons from Grenville quartzite 97ADK2. Error bars indicate ± 1 s.e. uncertainty in the mean. Analyses from grain interiors (filled circles) and the outermost 3 μm of crystal growth faces (open squares, $n = 48$ spot analyses) are shown (see Table 3). The zircon rims on growth faces have similar $\delta^{18}O$ values to metamorphic garnets in this rock (open triangle, $n = 5$ laser analyses) and are in isotopic equilibrium with host quartz. A total of 119 spot analyses for zircon by ion microprobe and five laser analyses of garnet are shown. The zircon interiors are highly variable, probably representing igneous provenance, and not in equilibrium with rims. Gradients of $\delta^{18}O$ of 6–8‰ are developed, apparently by exchange during metamorphism, and premetamorphic compositions are preserved in zircon cores.

possibility of thin rims of metamorphic zircon, REE contents were also determined for the crystal faces by ion microprobe. Rare-earth element contents of crystal growth faces are on the whole high, and vary from crystal to crystal (Fig. 8). Variable REE content suggests the absence of a metamorphic zircon overgrowth on analyzed crystals, as REE contents should be constant from sample to sample (for isolated detrital grains in a quartz matrix). In addition, metamorphic zircon grown in the quartzite should on average have low REE (reflecting the quartzite composition; see Maas et al. 1992) and depleted HREE in this garnet-bearing sample (Whitehouse and platt 2003). Thus, we interpret the variable and high REE contents to indicate that the zircon crystal faces are in fact igneous growth faces, modified in $\delta^{18}O$ by diffusion.

In sample 97ADK4, there is less contrast between $\delta^{18}O$ of crystal faces and the normal grain interiors than in 97ADK2 (Figs. 7 and 10). Zircon faces in 97ADK4 have identical $\delta^{18}O$ values to that of garnet from this sample (as observed in 97ADK2): $\delta^{18}O$(zircon faces) = 10.3 ± 1.1‰ ($n = 29$ spots, 1 s.e. = 0.2‰) and $\delta^{18}O$(garnet) = 9.9 ± 0.4‰ ($n = 4$, 1 s.e. = 0.2‰), also indicative of approach to oxygen-isotope equilibrium at the edges of zircon crystals during metamorphism. However, oxygen diffusion was slow enough to preserve gra-
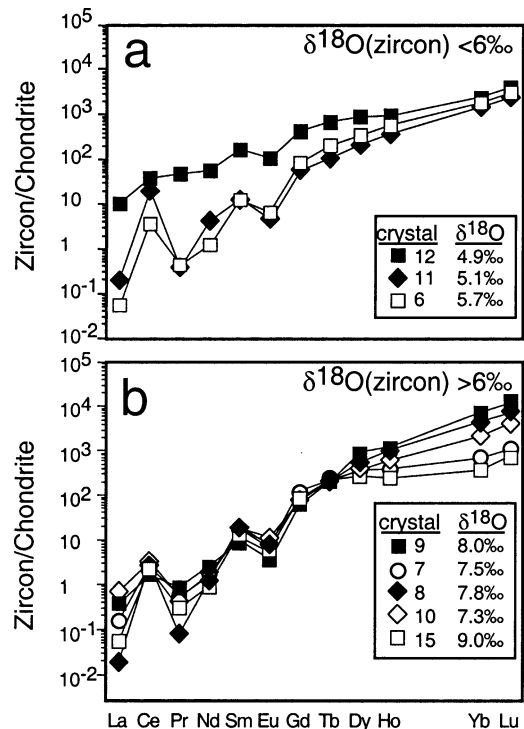

FIGURE 8. Ion-microprobe analyses of rare-earth element contents of crystal faces of detrital zircons from Grenville quartzite 97ADK2 (Peck 2000). Figure 8a shows grains with interior $\delta^{18}O$ <6‰, and Figure 8b shows grains with interior $\delta^{18}O$ >6‰. Variable REE content is due to sedimentary mixing of zircons from different igneous rocks and indicates the absence of a metamorphic zircon overgrowth on analyzed crystals. If REE compositions were metamorphic, they would be more constant from crystal to crystal.

dients up to 5‰ between relict cores and overgrowths in this sample.

Preservation of inherited $\delta^{18}O$ values in zircon cores. An additional test for oxygen diffusion rate within zircon is the analysis of oxygen isotope ratios in inherited magmatic cores. In 97ADK4, rounded cores are visible by CL in some samples (e.g., Fig 9). These cores have experienced a prolonged history as they are older than the magmatic overgrowth that is older than the metasediment (≥1.3 Ga). Four of these rounded cores have been analyzed by ion microprobe and have $\delta^{18}O$ values from 8.6 to 5.1‰, distinct from their crystal overgrowths (Table 3, Fig. 10). Preservation of these steep gradients in oxygen-isotope ratio supports slow oxygen diffusion during metamorphism. The preservation of oxygen-isotope heterogeneity in inherited cores (relative to the rest of the crystal) after igneous overgrowth and metamorphic annealing proves that diffusion of oxygen was very slow in these zircon crystals. The inherited cores of some zircon crystals are up to 5.6‰ lower in $\delta^{18}O$ than igneous overgrowths showing that gradients of over 5‰ per 50 µm can be preserved even at magmatic conditions.

Diffusion modeling: Size vs. $\Delta^{18}O$(quartz-zircon). We interpret the $\delta^{18}O$ values of detrital zircon crystals in quartzite to be the result of incomplete exchange with the host quartz during metamorphism for the following reasons. If diffusion had been relatively fast, as predicted by hydrothermal experiments (Watson and Cherniak 1997), two scenarios would be possible: (1) zircon crystals could become equilibrated completely and have been quenched; or (2) zicon crystals could have equilibrated and then continued to exchange with other minerals in the quartzite during cooling. In scenario 1, zircon crystals would have $\delta^{18}O$ values identical to garnet in the same rock, and the preceeding section has shown that this is not the case. In scenario 2, a negative relationship between Δ(Qtz-Zrc) and zircon size would be expected, reflecting different closure temperatures of different zircon sizes. Scenario 2 was evaluated using the Fast Grain Boundary (FGB) diffusion model of Eiler et al. (1992), using the FGB code of Eiler et al. (1994) with minor modifications by Kohn and Valley (1998a). In using the FGB model to assess scenario 2, we assumed oxygen-isotope equilibration at the peak of metamorphism, diffusive exchange through the crystal structure of minerals, and isotopic equilibrium along grain boundaries on the scale of several grain diameters (see Eiler et al. 1992, 1993). The exchange and resetting of oxygen-isotope ratios is calculated using mineral modes and grain sizes, peak metamorphic temperatures, cooling rates, fractionation factors, and oxygen diffusion rates (see Table 4). For these rocks, 1.5 °C/m.y. cooling after 675 °C Ottawan metamorphism (see Fig. 4) and the "wet" diffusion rate measured at $P_{H_2O} = 0.07$ to 10 kbar by Watson and Cherniak (1997) were used. The result is shown as a heavy curved line on Figure 6. Values of Δ(Qtz-Zrc) are much more variable among the samples in Figure 6 than predicted by the FGB model, implying that diffusion was sufficiently slow that the zircon crystals never reached isotopic equilibrium with their host rocks. Thus, the second scenario is not supported by the natural data either, and the heterogeneity that we report must be dominantly pre-metamorphic in origin.

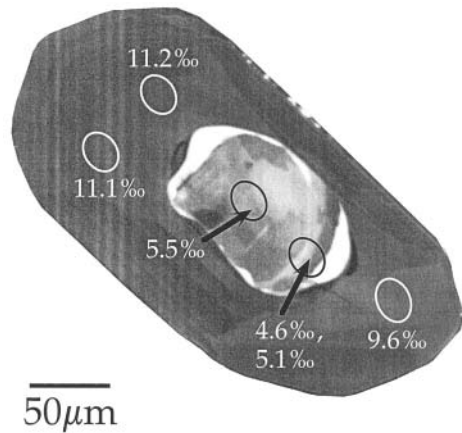**Diffusion modeling: $\delta^{18}O$(Large Zircon) vs. $\Delta^{18}O$(Large-**

FIGURE 9. CL image of detrital igneous zircon no. 9 from quartzite 97ADK4. Ion-microprobe analyses of $\delta^{18}O$ are shown. Note that the $\delta^{18}O$ of the inherited core is distinct from the $\delta^{18}O$ of the rest of the interior of the grain. Two of the analyses of the core were made without moving the microprobe stage between analyses.
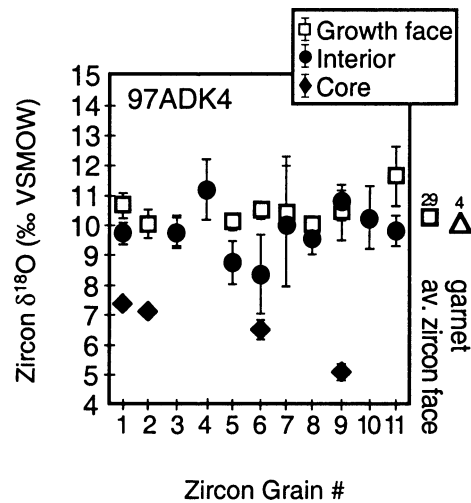

FIGURE 10. Ion-microprobe analyses of $\delta^{18}O$ from cores and rims in 11 individual detrital (magmatic) zircons from Grenville Quartzite 97ADK4. Error bars indicate ±1 s.e. uncertainty in the mean. Analyses from grain interiors (filled circles), inherited cores (filled diamonds) visible by CL, and crystal growth faces (open squares) are shown (see text). Open triangle = garnet. A total of 29 spot analyses for zircon by ion microprobe and four laser analyses of garnet are shown.

Small) Zircon. To constrain the amount of diffusive exchange experienced by detrital zircon crystals during metamorphism, isothermal diffusion calculations were made. For 97ADK2, the large interior to rim differences in $\delta^{18}O$ measured by ion microprobe suggest short diffusion gradients of up to 7‰ over short distances at the edge of the crystal. Furthermore, the data from size fractions of zircon allow the calculation of the diffusion rate that is consistent with the measured rim $\delta^{18}O$, the preservation of igneous core $\delta^{18}O$ values, and the $\delta^{18}O$ values of

TABLE 4. Oxygen diffusion rates and fractionation factors used in Fast Grain Boundary (FGB) diffusion modeling

Mineral	Q	D_o	Reference	A	Reference
Quartz	243	2.90E-1	6	0	–
Plagioclase	85	1.00E-9	1	1.15	4
K-feldspar	85	1.00E-9	1	0.94	4
Augite	226	1.50E-6	3	2.75	5
Magnetite	188	3.50E-6	2	6.29	5
Biotite	142	9.10E-6	7	2.16	8
Zircon (W)	210	5.50E-8	9	2.55	*10
Zircon (D)	448	1.33	9	2.55	*10

Note: Plagioclase is modeled as An_{20}. D_o (pre-exponential factor in cm^2s^{-1}) and Q (activation energy in $kJ\ mol^{-1}$) are from the Arrhenius relationship for the diffusion coefficient: $D = D_o exp(–Q/RT)$ where R is the gas constant and T is temperature (K). All diffusion data are from hydrothermal experiments except the anhydrous (D) experiments of Watson and Cherniak (1997). A-factors are for the formula $\Delta^{18}O(Qt-Mineral) \cdot A*10^6/T^2$. Mode % is modeled as quartzite ~100% quartz with trace zircon; syenite 14% plagioclase, 76% K-feldspar, 6% augite, and 4% magnetite with trace zircon; and granite 25% quartz, 14% plagioclase, 51% K-feldspar, 6% augite, and 4% magnetite with trace zircon.
References: 1 = Elphick et al. (1986), 2 = Giletti and Hess (1988), 3 = Farver (1989), 4 = Clayton et al. (1989), 5 = Chiba et al. (1989), 6 = Farver and Yund (1991), 7 = Fortier and Giletti (1991), 8 = Chacko et al. (1996), 9 = Watson and Cherniak (1997). 10 = Valley et al. (2003).
* Calculated using $\Delta(Zrc-Gt) = 0.0$, using the fractionation for almandine-pyrope garnet from Kohn and Valley (1998b) because it is appropriate for the garnet compositions in the lithologies studied, See Valley et al. 2003.
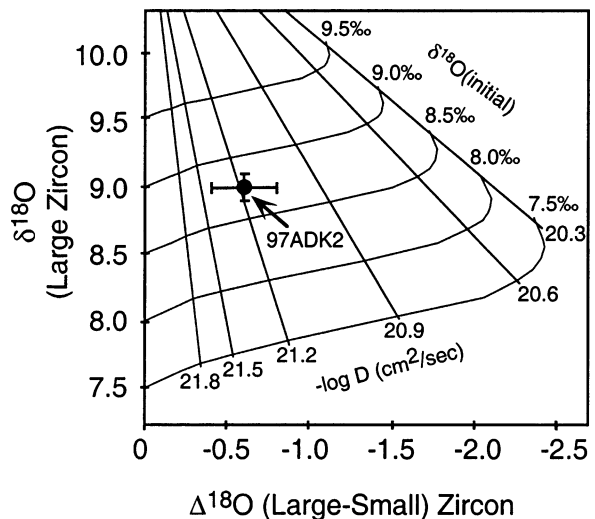

FIGURE 11. Calculation of isothermal oxygen diffusion in zircons from quartzite 97ADK2 [$\delta^{18}O$(quartz) = 13.6] with variable initial $\delta^{18}O$ and diffusion rate. It is assumed that, initially, zircon crystals were isotopically homogeneous. This calculation determines the values of initial $\delta^{18}O$ and oxygen diffusion rate consistent with measured values of $\delta^{18}O$ and $\Delta^{18}O$ between large and small zircon crystals in this sample. The $\delta^{18}O$ of the largest zircon crystals in 97ADK2 (9.0‰, diameter ≈ 180 μm) is plotted against the fractionation ($\Delta^{18}O$) between 180 μm and 60μm diameter crystals (~0.6‰), with ±1 s.d. error bars. Contours show varying initial $\delta^{18}O$ and oxygen diffusion rate. The contoured part of the figure shows the range of partial equilibration of zircon; the kink in contours at high diffusion rates marks the beginning of rapid exchange (toward equilibrium). The calculations were made for isothermal annealing at 600 °C for 25 m.y. The maximum diffusion rate consistent with measured data for this sample is ~6.3 × 10^{-22} cm^2/s (log D = –21.2 cm^2/s). Note that the predicted equilibrium $\delta^{18}O$(zircon) for the crystal growth face (11.2‰) is off of the figure, and it is implicit that most zircons preserve diffusion gradients in $\delta^{18}O$ after such annealing.

different size crystals. This calculation estimates the maximum possible diffusion rate because it assumes that measured heterogeneity is the result of diffusion. If, as is likely, the measured heterogeneity is pre-metamorphic (i.e., igneous zoning unmodified by diffusion), then the estimated upper limit on diffusion rate will be lower.

Diffusion profiles for different size zircon crystals were calculated using the non-steady-state solution for diffusion in a sphere with uniform initial composition and a fixed surface composition (Eq. 6.18 of Crank 1975). For 97ADK2, the measured rim composition of 11.2‰ was used (measured in crystal faces by ion microprobe as well as by laser in garnet). The diffusion rate (D) and initial $\delta^{18}O$(zircon) were varied (see Fig. 11). Diffusion was calculated for 25 m.y. at 600 °C, clearly a minimum for both temperature and time given the polymetamorphic history of these rocks and slow cooling after the granulite-facies Ottawan orogeny (Mezger et al. 1991; see Fig. 4). Thus, this calculation estimates the diffusion rate necessary to create the observed $\delta^{18}O$ for large and small zircon crystals at the lower estimates of temperature and time, yielding a maximum value of D. This is a conservative estimate; if metamorphic parameters were better known, the true maximum D would be lower than we estimate.

Figure 11 shows the results of this calculation while varying diffusion rate and initial $\delta^{18}O$(zircon) values, assuming that all zircons are homogenized and have the same $\delta^{18}O$. The $\delta^{18}O$ of the largest zircon crystals in 97ADK2 is plotted against the fractionation between the largest and smallest zircon for bulk analyses by laser Fluorination. The measured values of $\delta^{18}O$(zircon) and the fractionation between zircon crystals of different size in this sample are best modeled by an initial $\delta^{18}O$(zircon) of ~8.7‰ and a maximum diffusion rate for oxygen in zircon of ~6.3 × 10^{-22} cm^2/s (log D = –21.2 cm^2/s on Fig. 11).

The four other quartzite samples with three or more ana-

lyzed zircon splits were also modeled, and yielded similar constraints on diffusion rates (Fig. 12). Note that each sample could be plotted in a figure similar to Figure 11, but the different input variables to the calculation preclude plotting all five samples on the same figure. The peak metamorphic temperatures vary among sampling localities, as do the constraints on cooling rates after peak metamorphism. Modeling parameters were selected to be conservative given the constraints on temperature-time history (after Bohlen et al. 1985; Mezger et al. 1991). Samples 97ADK3 and 97ADK4 were modeled for 25 m.y. at 600 °C, and yielded upper limits on diffusion rate of 2.5 × 10^{-22} and 1.2 × 10^{-22} cm^2/s, respectively. Sample 97ADK4 has the most limiting constraints on diffusion rate of any quartzite sample, given the lack of correlation between grain size and $\delta^{18}O$ and the good reproducibility of the $\delta^{18}O$ measurements. Sample 92ADK 7 was modeled using 40 m.y. at 600 °C, and yielded an upper limit on the oxygen diffusion rate of 1.6 × 10^{-22} cm^2/s. The high temperature thermal history of the Frontenac terrane (where 97WE10 was collected) is not well-constrained, but slow cooling after metamorphism and monazite closure to
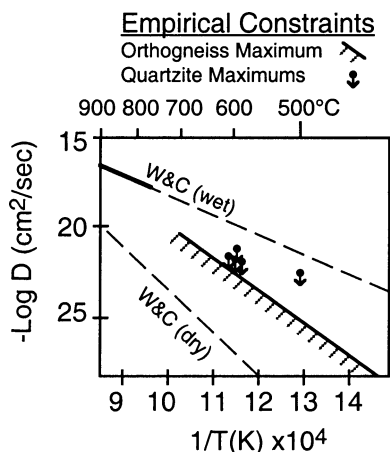
Empirical Constraints
Orthogneiss Maximum
Quartzite Maximums

FIGURE 12. Arrhenius plot of experimentally determined oxygen diffusion rates in zircon from hydrothermal "W&C (wet)" and anhydrous "W&C (dry)" experiments (Watson and Cherniak 1997). Dark line shows range of experimental temperatures, short dashes are extrapolation. Also shown are the empirical maximum diffusion rates from this study determined from $\delta^{18}O$(zircon) vs. crystal size relationships by laser fluorination and ion-microprobe analysis of zircons from slowly cooled amphibolite- and granulite-facies orthogneiss and quartzites.

U-Pb diffusion (Mezger et al. 1991) allow calculation of oxygen diffusion in this sample for 50 m.y. at 500 °C. The upper limit on the diffusion rate of oxygen in zircon for this sample is 3.2×10^{-23} cm^2/s.

Note that temperature is not a part of the diffusion calculation but is used for plotting the Arrhenius diagram; the effect of varying the assumed annealing temperature can be inspected on Figure 12. If the metamorphic temperatures of ~750 °C from recent work (Storm and Spear 2002) are used for Adirondack quartzites instead of the 675–725 °C of Bohlen et al. (1985), then the maximum diffusion rates calculated here would be lower and closer to the values from anhydrous diffusion experiments (Watson and Cherniak 1997). For example, for sample 97ADK2 at 600 °C (see modeling parameters above), D_{max} is 1.4 log units slower than the hydrothermal experiments of Watson and Cherniak (1997). If this maximum diffusion rate is taken at 750 °C, D_{max} is 3.2 log units slower than the hydrothermal experiments of Watson and Cherniak (1997).

GRENVILLE ORTHOGNEISS

Zircon crystals from dated metaplutonic rocks were analyzed to assess the amount of post-metamorphic oxygen diffusion in samples from the Adirondack Highlands (Fig. 3). These zircon crystals range in age from >1336 to 1095 Ma, and span the history of magmatism and metamorphism in the Adirondacks (Fig. 4). Geochronology and descriptions of these samples are detailed in McLelland et al. (1988), McLelland and Chiarenzelli (1991), and Chiarenzelli and McLelland (1991), and are described briefly here. Tonalite LDT has disturbed U-Pb systematics, and gives a minimum age of 1336 Ma, in the earliest phase of Adirondack crust building (before the ca. 1200 Ma Elzevirian orogeny). Granitic gneiss TOE gives a minimum age of 1184 Ma, which is also consistent with em-

placement before the Elzevirian orogeny. Two samples (AM86-8, 98LB3) belong to the voluminous 1155 ± 10 Ma anorthosite-mangerite-charnockite-granite (AMCG) suite in the Adirondacks. Charnockite AM86-8 has a minimum age of 1084 Ma, and is petrologically related to other AMCG lithologies. Metasyenite 98LB3 is undated, but is part of the ca. 1155 Ma Diana complex. Samples NOFO-1 and AM86-6 belong to the Hawkeye granites, a younger suite of deformed granitic rocks, and are dated 1095 ± 5 Ma and 1098 ± 4 Ma, respectively. NOFO-1 also contains a minor population of 1155 Ma zircon xenocrysts. Figure 4 illustrates the chronology of these samples and major thermal events that they experienced. All of these samples were metamorphosed during the 1035–1090 Ma Ottawan orogeny (McLelland et al. 2001), and experienced peak temperatures of 700 to 800 °C at water fugacities >1000 bar (Bohlen et al. 1985; Storm and Spear 2002), followed by slow cooling (1–3 °/My; Mezger et al. 1991). Different sizes of zircon (Table 1) were analyzed from all samples, and all samples except LDT fail to show systematic relationship between size and $\delta^{18}O$(zircon). Zircon crystals from LDT span ~0.6‰, but the smallest zircon split has the heaviest oxygen isotope ratios (Fig. 13). Values of $\delta^{18}O$(zircon) from these rocks are typical of zircon crystals from other rocks of their respective Adirondack suites (Valley et al. 1994, Peck et al. 2000).

Modeling of diffusive oxygen exchange after metamorphism of orthogneiss can offer constraints on oxygen diffusion rates when compared with observed variations among crystals of different size. Inter-mineral oxygen diffusion during cooling was modeled with the FGB diffusion model of Eiler et al. (1992) (see above for details of the model). Note that in this case, initial oxygen-isotope equilibrium is also assumed, as is appropriate for these metaigneous rocks.

FGB modeling of a granite and a syenite using data from the wet experiments of Watson and Cherniak (1997) for 1.5 °C/m.y. cooling after 675 °C Ottawan metamorphism (see Fig. 4) predicts a measurable fractionation between zircon crystals of different sizes (Fig. 13). Note that a more siliceous rock causes more dispersion in $\delta^{18}O$(zircon) versus crystal size due to exchange with quartz and feldspar, which have large fractionations with zircon at low temperatures. Therefore, the calculated trend for syenite predicts smaller fractionations between large and small zircon crystals, and is a conservative calculation. FGB calculations using five different hypothetical values for oxygen diffusion rates for zircon for the cooling syenite are shown on Figure 14.

In the orthogneiss samples, as in the quartzite, FGB diffusion modeling using "wet" diffusion rates predicts that small zircon crystals should develop lower $\delta^{18}O$ values during slow cooling after granulite-facies metamorphism. Thus, post-metamorphic exchange would result in a negative slope on Figures 13 and 14, along a specific curve depending on the actual diffusion rate. Sample LDT has the opposite relation, a negative correlation between zircon size and $\delta^{18}O$ (positive slope on Fig. 13). This finding is not consistent with diffusive exchange during slow cooling. Furthermore, none of the zircon samples show the absolute values predicted for diffusive exchange during slow cooling after Ottawan metamorphism (which they all experienced) for diffusion models faster than model 5 (Fig. 14). In-
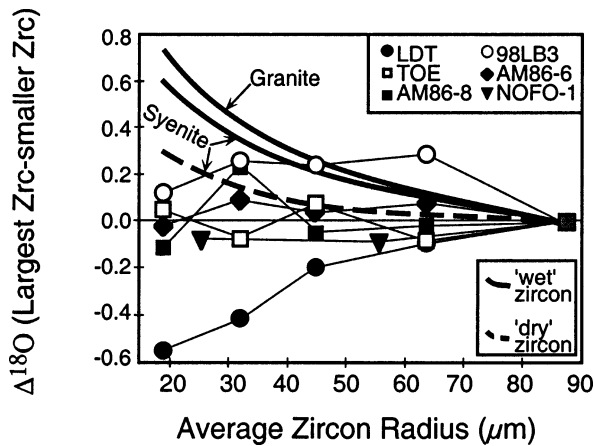
FIGURE 13. Oxygen-isotope fractionation between different size zircons from Grenville orthogneiss. Predicted $\delta^{18}O$ values from FGB diffusion modeling are also shown for "wet" (heavy lines, syenite and granite) and "dry" (dashed line, syenite) experimental diffusion rates (see text). No systematic relation between $\delta^{18}O$ and zircon grain size is seen among measured data, indicating slow oxygen diffusion during cooling after granulite-facies metamorphism.

FIGURE 14. Diffusion models for slow cooling of Adirondack syenitic orthogneiss. The five model values of diffusion were chosen to bracket the experimentally determined values of "wet" diffusion. For fast rates of oxygen diffusion in zircon, a strong dependence between grain size and $\delta^{18}O$ should develop. This dependence is not observed in the data on Figure 13, indicating slow oxygen diffusion during cooling after granulite-facies metamorphism.

stead, the oxygen-isotope ratios of most samples are within ~0.4‰ of each other.

At diffusion rates faster than model 5, the fractionation between the largest and smallest zircon crystals should be >0.4‰. Systematic variation in $\delta^{18}O$ between large and small zircon crystals of greater than 0.4‰ would be resolvable in our data given the reproducibility of the analyses (Table 1). This variation is not observed, indicating oxygen diffusion rates slower than model 5.

DISCUSSION

How do experiments compare to empirical data on oxygen diffusion?

The relevance and application of the results of water-saturated oxygen diffusion experiments to conditions of high-grade metamorphism are complicated because the exact mechanisms of oxygen diffusion in minerals under "wet" or "dry" conditions remain uncertain (e.g., Graham and Elphick 1994; Cole and Chakraborty 2001). Furthermore, the precise meaning of "wet" and "dry" in relation to high-grade metamorphism requires careful definition. Water fugacity, f_{H_2O}, calculated from mineral-fluid equilibria, is a useful indicator of the role of water in metamorphic rocks. Assuming ideality, $f_{H_2O} \times a_{H_2O} \times P_{H_2O}$. If f_{H_2O} is the controlling variable for oxygen diffusion (e.g., Farver and Yund 1991), then the comparison between rocks and experiments is straightforward. However, Watson and Cherniak (1997) did not find a dependence of oxygen diffusion in zircon on the value of P_{H_2O} or f_{H_2O}. The mechanism of oxygen diffusion may involve H_2O as a carrier species (Farver and Yund 1991), or protons as activating species (Elphick and Graham 1988) within the crystal structure. In the case of protons, there may be a (possibly low) threshold level of H-bearing species below which diffusion may be much slower than in
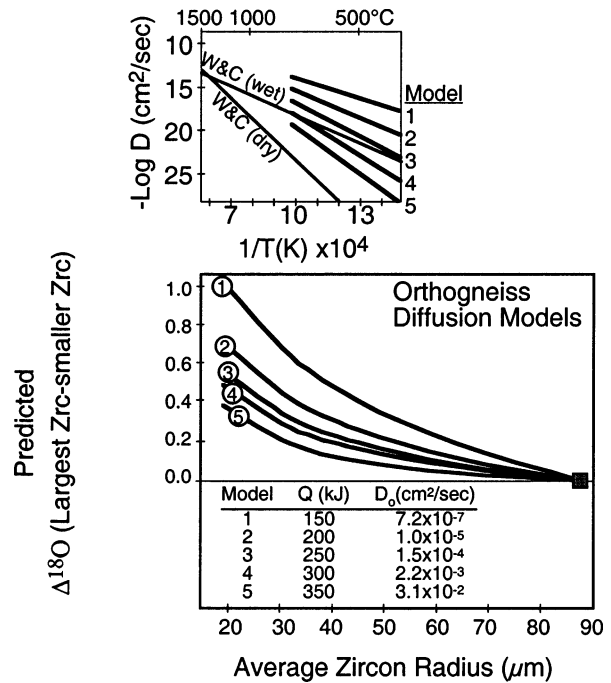
an H_2O-rich environment and proceeds by a quite different (intrinsic vs extrinsic) mechanism. If the mechanism of oxygen diffusion involves H_2O as a carrier species within the crystal lattice, then diffusion in a fluid-absent environment may be significantly slower than if an H_2O-bearing fluid is present, even if values of f_{H_2O} are equivalent. Experiments to evaluate this possibility are under way (B. Watson, pers. comm. Nov. 2002).

Given the high confining pressures (~8 kbar) of Adirondack metamorphism, values of f_{H_2O} suggest that the "wet" experiments are appropriate for modeling conditions of peak metamorphism. Granulite-facies rocks are commonly referred to as "dry," but more precisely, they have low water activities (for example, granulite-facies orthogneiss from the Adirondack Highlands have a_{H_2O} estimated as low as 0.1–0.2; Valley et al. 1990). At the peak of granulite-facies metamorphism (~8 kbar), an activity of 0.1–0.2 corresponds to water fugacities of >1000 bar much higher than the 70 bar in the "wet" experiments. All the biotite- or amphibole-bearing metaigneous rocks studied had peak water fugacities at least an order of magnitude higher than 70 bar.

It is likely that quartzites also were metamorphosed at f_{H_2O} > 70 bar. Although water fugacities in these lithologies are difficult to constrain, there is no simple mechanism that would desiccate these originally water-saturated metasediments; compaction and dehydration remove H_2O, but do not by them-

selves reduce a_{H_2O}. Although the cause of this apparent discrepancy between empirical and experimental data is not understood, we make the following observations about the significance.

The lack of strong correlations between zircon size and $\delta^{18}O$ in orthogneiss and quartzite is not consistent with diffusion calculations using "wet" oxygen diffusion rates in zircon that yield closure temperatures on the order of 500–550 °C, and is more consistent with closure temperatures ≥700 °C. The observed disequilibrium between zircon cores and interiors, and among zircon crystals in the same rock also argues for oxygen diffusion rates slower than "wet" values ($< \sim 10^{-22}$ cm^2/s), and are more consistent with the diffusion rates from "dry" experiments (see Fig. 12) and from the increment method (Zheng and Fu 1998).

Implications for diffusion modeling

For minerals with closure temperatures below or near the peak temperature of interest, accurate knowledge of oxygen diffusion rates is essential for the meaningful interpretation of oxygen-isotope results. In some studies, the goal is to determine if minerals in high-grade rocks preserve premetamorphic $\delta^{18}O$ values, whereas in other studies, determining the peak metamorphic $\delta^{18}O$ is the goal (see Valley 2001).

Systematic resetting of oxygen isotope ratios is sometimes used to infer cooling rates in metamorphic rocks. If the "wet" experimental diffusion rates are assumed for zircon, the lack of $\delta^{18}O$ dependence on zircon grain-size in metaigneous rocks (such as seen in this study) could erroneously be taken to indicate rapid cooling in a slowly cooled metamorphic terrane. The "wet" diffusion rates also might be used to mistakenly infer peak metamorphic temperatures <500 °C from the oxygen-isotope variability between crystals in a metamorphic rock (as is seen in Adirondack and Frontenac detrital zircons). In the absence of other constraints on metamorphism, the use of inappropriate oxygen diffusion rates could clearly cause metamorphic conditions to be miscalculated in high-grade rocks.

Numerical models that predict oxygen-isotope resetting during cooling generally use experimental diffusion rates as a primary input parameter (e.g., Giletti 1986; Eiler et al. 1992; Kohn 1999). Peak temperatures in rocks that have experienced retrograde oxygen diffusion are often estimated by "backing out" the effects of diffusion (e.g., Farquhar et al. 1993). In the case of zircon, the use of "wet" experimental diffusion rates would cause the overestimation of retrogressive oxygen exchange during slow cooling, and therefore peak temperatures calculated in this way could erroneously be higher than actual peak temperatures.

Water fugacity during cooling

Kohn (1999) proposed that minerals in most metamorphic rocks continuously re-equilibrate and buffer their water fugacity during cooling and retrogression. In this model, water fugacities are estimated based on mineral equilibria at declining temperature and pressure during cooling and uplift, assuming instantaneous mineral equilibrium. These water fugacities are used to calculate oxygen diffusion rates with equations derived from diffusion experiments. Oxygen diffusion rates in zircon

at high temperature are predicted to be significantly faster than those in the "wet" experiments, which were conducted at higher P_{H_2O} (70 to 10 000 bar). For example, the apparent diffusion rate for zircon in the driest rock considered by Kohn is shown on Figure 1 (a metabasite cooled from 750 °C, 8 kbar, and initial $a_{H_2O} = 0.15$). The oxygen diffusion rate calculated at 800 °C for this rock is 950 times faster than diffusion calculated from the "wet" experiments of Watson and Cherniak (1987). If diffusivities this fast had been experienced by any of the zircon crystals in metaigneous and metasedimentary rocks examined in the present study, then premetamorphic $\delta^{18}O$ values would be lost, and strong $\delta^{18}O$ vs. grain size correlations would be apparent. The oxygen diffusion rates estimated from our study are not consistent with such fast diffusion. The maximum diffusion rate of oxygen in zircon in the samples studied is lower, possibly much lower, than ca. 10^{-22} cm^2/s at 600 °C. This is slower than the relatively fast, hydrothermally determined values but is consistent with anhydrous experiments (Watson and Cherniak 1997).

REFERENCES CITED

Anders, E. and Grevesse, N. (1989) Abundances of the elements: Meteoric and solar. Geochimica et Cosmoschimica Acta, 53, 197–214.

Anovitz, L.M. and Essene, E.J. (1990) Thermobarometry and pressure-temperature paths in the Grenville Province of Ontario. Journal of Petrology, 31, 197–241.

Bindeman, I.N. and Valley, J.W. (2001) Low-$\delta^{18}O$ rhyolites from Yellowstone: Magmatic evolution based on analyses of zircons and individual phenocrysts. Journal of Petrology, 42, 1491–1517.

Bohlen, S.R., Valley, J.W., and Essene, E.J. (1985) Metamorphism in the Adirondacks I, Petrology, pressure and temperature. Journal of Petrology, 26, 971–992.

Brady, J. B. (1995) Diffusion data for silicate minerals, glasses, and liquids: in T.H. Ahrens, editor, Mineral Physics and Crystallography: A Handbook of Physical Constants, AGU Reference Shelf 2, American Geophysical Union, p. 269–290.

Chiarenzelli, J.R. and McLelland, J.M. (1991) Age and regional relationships of granitoid rocks of the Adirondack Highlands. Journal of Geology, 99, 571–590.

Chacko, T., Hu, X., Mayeda, T.M., Clayton, R.N., and Goldsmith, J.R. (1996) Oxygen isotope fractionations in muscovite, phlogopite, and rutile. Geochimica et Cosmochimica Acta, 60, 2595–2608.

Chiba, H., Chacko, T., Clayton, R.N., and Goldsmith, J.R. (1989) Oxygen isotope fractionations involving diopside, forsterite, magnetite, and calcite; application to geothermometry. Geochimica et Cosmochimica Acta, 53, 2985–2995.

Clayton, R.N., Goldsmith, J.R., and Mayeda, T.K. (1989) Oxygen isotope fractionation in quartz, albite, anorthite, and calcite. Geochimica et Cosmochimica Acta, 53, 725–733.

Cole, D.R. and Chakraborty, S. (2001) Rates and mechanisms of isotopic exchange. In Valley J.W., and Cole D.R., Eds., Stable Isotope Geochemistry, 43, 83–224. Reviews in Mineralogy and Geochemistry, Mineralogical Society of America, Washington, D.C.

Crank, J. (1975) The mathematics of diffusion, 414 p. Clarendon Press, Oxford.

Crocombette, J.-P. (1999) Theoretical study of point defects in crystalline zircon. Physics and Chemistry of Minerals, 27, 138–143.

Dodson, M. (1973) Closure temperature in cooling geochronological and petrological systems. Contributions to Mineralogy and Petrology, 40, 259–274.

Edwards, K.J. and Valley, J.W. (1998) Oxygen isotope diffusion and zoning in diopside: the importance of water fugacity during cooling. Geochimica et Cosmochimica Acta, 62, 2265–2277.

Eiler, J.M., Baumgartner, L.P., and Valley, J.W. (1992) Intercrystalline stable iso-

tope diffusion: a fast grain boundary model. Contributions to Mineralogy and Petrology, 112, 543–557.

Eiler, J.M., Valley, J.W., and Baumgartner, L.P. (1993) A new look at stable isotope thermometry. Geochimica et Cosmochimica Acta, 57, 2571–2583.

Eiler, J.M., Baumgartner, L.P., and Valley, J.W. (1994) Fast grain boundary; a For-tran-77 program for calculating the effect of retrograde interdiffusion of stable isotopes. Computers and Geosciences, 20, 1415–1434.

Elphick, S.C. and Graham, C.M. (1988) The effect of hydrogen on oxygen diffusion in quartz: evidence for fast proton transients? Nature, 335, 243–245.

Elphick, S.C., Dennis, P.F., and Graham, C.M. (1986) An experimental study of the diffusion of oxygen in quartz and albite using an overgrowth technique. Contri-butions to Mineralogy and Petrology, 92, 322–330.

Farquhar, J., Chacko, T., and Frost, B.R. (1993) Strategies for high temperature oxygen isotope thermometry: a worked example from the Laramie anorthosite complex, Wyoming, USA. Earth and Planetary Science Letters, 117, 407–422.

Farver, J.R. (1989) Oxygen self-diffusion in diopside with application to cooling rate determinations. Earth and Planetary Science Letters, 92, 386–396.

Farver, J.R. and Yund, R.A. (1991) Oxygen diffusion in quartz; dependence on tem-perature and water fugacity. Chemical Geology, 90, 55–70.

Fortier, S.M. and Giletti, B.J. (1989) An empirical model for predicting diffusion coefficients in silicate minerals. Science, 245, 1481–1484.

——— (1991) Volume self-diffusion of oxygen in biotite, muscovite, and phlogo-pite micas. Geochimica et Cosmochimica Acta, 55, 1319–1330.

Giletti, B.J. (1986) Diffusion effects on oxygen isotope temperatures of slowly cooled igneous and metamorphic rocks. Earth and Planetary Science Letters, 77, 218–228.

Giletti, B.J. and Hess, K.C. (1988) Oxygen diffusion in magnetite. Earth and Plan-etary Science Letters, 89, 115–122.

Gilliam, C.E. and Valley, J.W. (1997) Low $\delta^{18}O$ magma, Isle of Skye, Scotland; evidence from zircons. Geochimica et Cosmochimica Acta, 61, 4975–4981

Graham, C.M., and Elphick, S.C. (1991) Some experimental constraints on the role of hydrogen in oxygen and hydrogen diffusion and Al-Si interdiffusion in sili-cates. In Ganguly, J., Ed., Diffusion and Flow in Minerals and Fluids, Advances in Physical Geochemistry 8, 238–285.

King, E.M., Barrie C.T., and Valley, J.W. (1997) Hydrothermal alteration of oxygen isotope ratios in quartz phenocrysts, Kidd Creek Mine, Ontario: Magmatic val-ues are preserved in zircon. Geology, 25, 1079–1082.

King, E.M., Valley, J.W., Davis, D.W., and Edwards, G.R. (1998) Oxygen isotope ratios of Archean plutonic zircons from granite greenstone belts of the Superior Province: indicator of magmatic source. Precambrian Research, 92, 365–387.

Kohn, M.J. (1999) Why most "dry" rocks should cool "wet". American Mineralo-gist, 84, 570–580.

Kohn, M.J. and Valley, J.W. (1998a) Obtaining equilibrium oxygen isotope fractionation from rocks. Theory and examples. Contributions to Mineralogy and Petrology, 132, 209–224.

Kohn, M.J. and Valley, J.W. (1998b) Effects of cation substitutions in garnet and pyroxene on equilibrium oxygen isotope fractionations. Journal of Metamor-phic Geology, 16, 625–639.

Maas, R., Kinny, P.D., Williams, I.S., Froude, D.O., and Compston, W. (1992) The Earth's oldest known crust: A geochronological and geochemical study of 3900-4200 Ma old detrital zircons from Mt. Narryer and Jack Hills, Western Austra-lia. Geochimica et Cosmochimica Acta, 56, 1281–1300.

McLelland, J.M. and Chiarenzelli, J.R. (1991) Geochronological studies in the Adirondack Mountains and the implications of a Middle Proterozoic tonalitic suite, in Gower, C.F., Rivers, T., and Ryan, B., eds., Mid-Proterozoic Laurentia-Baltica. Geological Society of Canada Special Paper 38, p. 175–194.

McLelland, J., Chiarenzelli, J., Whitney, P. and Isachsen, Y. (1988) U-Pb geochro-nology of the Adirondack Mountains and implications for their geologic evolu-tion. Geology, 16, 920–924.

McLelland, J., Hamilton, M., Selleck, B., McLelland, J., Walker, D., Orrell, S. (2001) Zircon U-Pb geochronology of the Ottawa Orogeny, Adirondack Highlands, New York: regional and tectonic Implications. Precambrian Research, 109, 39–72.

Mezger, K., Rawnsley, C.M., Bohlen, S.R., and Hanson, G.N. (1991) U-Pb garnet, sphene, monazite, and rutile ages: Implications for the duration of high grade metamorphism and cooling histories, Adirondack Mts., New York. Journal of Geology, 99, 415–428.

Monani, S. and Valley, J.W. (2001) Oxygen isotope ratios of zircon; magma genesis of low $\delta^{18}O$ granites from the British Tertiary igneous province, western Scot-land. Earth and Planetary Science Letters, 184, 377–392.

Muehlenbachs, K. and Kushiro, I. (1974) Measurements of oxygen diffusion in silicates. EOS Transactions of the American Geophysical Union, 56, 459.

Peck, W.H. (2000) Oxygen Isotope Studies of Grenville Metamorphism and Magmatism, Ph. D. Thesis, University of Wisconsin (Madison, WI), 320 p.

Peck, W.H., King, E.M., and Valley, J.W. (2000) An Oxygen Isotope Perspective on Precambrian Crustal Growth and Maturation. Geology, 28, 363–366.

Peck, W.H., Valley, J.W., Wilde, S. and Graham, C.M. (2001) Oxygen isotope ratios and rare earth elements in 3.3 to 4.4 Ga zircons: Ion microprobe evidence for high $\delta^{18}O$ continental crust and oceans in the Early Archean, Geochimica et Cosmochimica Acta, 65, 4215–4229.

Sager-Kinsman, E.A. and Parrish, R.R. (1993) Geochronology of detrital zircons from the Elzevir and Frontenac terranes, Central Metasedimentary Belt, Grenville Province, Ontario. Canadian Journal of Earth Sciences, 30, 465-473.

Storm, L.C. and Spear, F.S. (2002) Thermometry, cooling rates, and monazite ages of the Southern Adirondacks, Geological Society of America Abstracts with Pro-grams, 34(1), 6.

Sharp, Z.D. (1991) Determination of oxygen diffusion rates in magnetite from natu-ral isotopic variations. Geology, 19, 653–656.

Sharp, Z.D. and Jenkin, G.R.T. (1994) An empirical estimate of the diffusion rate of oxygen in diopside. Journal of Metamorphic Geology, 12, 89–97.

Valley, J.W. (2001) Stable isotope thermometry at high temperatures. In Valley J.W. and Cole D.R., eds. Stable Isotope Geochemistry: Mineralogical Society of America Reviews in Mineralogy and Geochemistry 43, 365–413.

——— (2003) Oxygen isotopes in zircon. In J. Hanchar and P. Hoskin, Eds., Zir-con, in press. Reviews in Mineralogy and Geochemistry, Mineralogical Society of America, Washington, D.C.

Valley, J.W. and Graham, C.M. (1991) Ion microprobe analysis of oxygen isotope ratios in granulite-facies magnetites, Diffusive exchange as a guide to cooling history. Contributions to Mineralogy and Petrology, 124, 225–234.

Valley, J.W., Bohlen, S.R., Essene, E.J., and Lamb, W. (1990) Metamorphism in the Adirondacks II, The role of fluids. Journal of Petrology, 31, 555–596.

Valley, J.W, Chiarenzelli, J.R., and McLelland, J.M. (1994) Oxygen isotope geochem-istry of zircon. Earth and Planetary Science Letters, 126, 187–206.

Valley, J.W., Kitchen, N., Kohn, M.J., Niendorf, C.R., and Spicuzza, M.J. (1995) UWG-2, a garnet standard for oxygen isotope ratios: Strategies for high preci-sion and accuracy with laser heating. Geochimica et Cosmochimica Acta 59, 5223–5231.

Valley, J.W., Graham, C.M., Harte, B., Eiler, J.M., and Kinny, P.D. (1998a) Ion microprobe analysis of oxygen, carbon, and hydrogen isotope ratios. In M.A. McKibben, W.C. Shanks, and W.I. Ridley, Eds., Reviews in Economic Geol-ogy 7, 73–98. Society of Economic Geologists, Littleton, Colorado.

Valley, J.W., Kinny, P.D., Schulze, D.J., and Spicuzza, M.J. (1998b) Zircon megacrysts from kimberlite; oxygen isotope variability among mantle melts. Contributions to Mineralogy and Petrology, 133, 1–11.

Valley, J.W., Bindeman, I.N., and Peck W.H. (2003) Empirical calibrations of oxy-gen isotope fractionation in zircon. Geochimica et Cosmochimica Acta, in press.

Watson, E.B. and Cherniak, D.J. (1997) Oxygen diffusion in zircon. Earth and Plan-etary Science Letters, 148, 527–544.

Weiner, R.W., McLelland, J.M., Isachsen, Y.W., and Hall, L.W. (1984) Stratigraphy and structural geology of the Adirondack Mountains, New York: Review and synthesis. In M.J. Bartholomew, Ed., The Grenville event in the Appalachians and related topics, 194, p. 1–55. Geological Society of America Special Paper.

Whitehouse, M.J. and Platt, J.P. (2003) Dating high-grade metamorphism-constraints from rare-earth elements in zircon and garnet. Contributions to Mineralogy and Petrology, 145, 61–74.

Zheng, Y-F. and Fu, B. (1998) Estimation of oxygen diffusivity from anion porosity in minerals. Geochemical Journal, 32, 71–89.