



PII S0016-7037(01)00639-1

Empirical determination of oxygen isotope fractionation factors for titanite with respect to Zircon and Quartz

ELIZABETH M. KING,^{1,*}† JOHN W. VALLEY,¹ DON W. DAVIS,² and BART J. KOWALLIS³

¹Department of Geology and Geophysics, 1215 West Dayton Street, University of Wisconsin, Madison, WI 53706, USA

²Department of Mineralogy and Geology, Royal Ontario Museum, 100 Queen's Park, Toronto, Ontario, M5S 2C6, Canada

³Department of Geology, Brigham Young University, Provo, UT 84602, USA

(Received October 26, 2000; accepted in revised form March 19 2001)

Abstract—Measurements of oxygen isotope fractionations between coexisting igneous titanite (Ttn) and zircon (Zrc) have been used to formulate a self-consistent, empirical calibration of equilibrium oxygen isotope partitioning:

$$1000 \ln\alpha(\text{Zrc} - \text{Ttn}) = 1.02 \times 10^6/(T^2)$$

This calibration is based on the average measured $\Delta(\text{Zrc-Igneous Ttn}) = 1.2 \pm 0.3\%$ ($n = 27$ rocks) and a closure temperature of titanite to oxygen diffusion of approximately 650°C. The average measured fractionation between zircon and metamorphic titanite is $2.1 \pm 0.4\%$ ($n = 5$ rocks). These results show that $\Delta(\text{Zrc-Ttn})$ can be used to distinguish igneous vs. metamorphic (or hydrothermal) titanite.

The new zircon-titanite fractionation has been combined with published experimental and empirical data to provide a new quartz-titanite fractionation curve:

$$1000 \ln\alpha(\text{Qtz} - \text{Ttn}) = 3.57 \times 10^6/(T^2)$$

This new calibration is consistent with $\Delta(\text{Qtz-Igneous Ttn})$ data from coexisting mineral pairs in granitic rocks. Modeling diffusional exchange of oxygen during cooling in a typical granitic rock, using the new calibration, results in the same $\Delta(\text{Qtz-Igneous Ttn})$ as measured ($4.5 \pm 0.43\%$, $n = 25$ rocks). Both measured $\Delta(\text{Zrc-Igneous Ttn})$ and $\Delta(\text{Qtz-Igneous Ttn})$ differ from fractionations calculated using the semiempirical increment method. The consistency of empirical $\Delta(\text{Zrc-Igneous Ttn})$ in a range of geologic environments allows the calculation of a more accurate fractionation factor for titanite. *Copyright © 2001 Elsevier Science Ltd*

1. INTRODUCTION

Titanite and zircon are important accessory minerals for isotope geochemistry in many igneous and metamorphic rocks. The refractory nature of titanite and zircon, and the incorporation of Th and U in the crystal lattice, allow these minerals to be used for U-Pb geochronology. As a result of being a relatively reactive mineral, the U-Pb age of titanite could be indicative not only of igneous events, but also metamorphic and hydrothermal events (Frost et al., 2000). Trace element compositions, particularly Th/U ratios, can also distinguish igneous from metamorphic titanite. Metamorphic titanite typically has Th/U ratios less than 2.2 due to the solubility of UO_2^{2+} and the immobility of Th in fluids (Abraham et al., 1994; Frost et al., 2000). Zircon has been shown to be capable of retaining magmatic oxygen isotope ratios through metamorphic or hydrothermal events (Gilliam and Valley, 1997; King et al., 1997; King et al., 2000; King et al., 1998; Monani and Valley, 2001; Peck et al., 1999; Valley et al., 1994). The oxygen isotope fractionations of titanite, however, have not been empirically determined, only semiempirically using the increment method (Hoffbauer et al., 1994; Zheng, 1993). The use of $\delta^{18}\text{O}$ to

distinguish igneous from metamorphic or hydrothermal titanite assemblages would provide important information about a rock's history, and potentially about the $\delta^{18}\text{O}$ of magmas, and could guide geochronology studies (Wickham et al., 1996). The typically larger grain size and abundance of titanite relative to zircon makes titanite an appealing mineral to work with, provided the oxygen isotope fractionations can be well calibrated. Titanite $\delta^{18}\text{O}$ could also be important for obtaining magmatic $\delta^{18}\text{O}$ values in rocks that do not contain zircon.

Empirical calibrations are only accurate if diffusion of oxygen through the crystal lattice is not fast enough to significantly reset oxygen isotope ratios in a given mineral. Experiments at water saturated conditions ($\text{PH}_2\text{O} \approx 1\text{kbar}$, "wet") suggest that diffusion rates of oxygen in zircon and titanite are similarly slow. Wet diffusion rates of oxygen in titanite are slower than for most common igneous minerals (Fig. 1) (Morishita et al., 1996) and similar to wet diffusion rates of zircon (Watson and Cherniak, 1997). Rates of oxygen diffusion in titanite under anhydrous conditions have not been determined. Dry diffusion rates in zircon are significantly slower than wet diffusion rates (Watson and Cherniak, 1997) (Fig. 1).

A titanite crystal with a radius of 500 μm has a closure temperature of approximately 650°C, using wet diffusion data with a cooling rate of 10°C/Ma (Dodson, 1973; Morishita et al., 1996). For comparison, the closure temperature of quartz under hydrothermal conditions with the same cooling rate and a

*Author to whom correspondence should be addressed (emking@ilstu.edu).

† Present address: Department of Geography - Geology, Illinois State University, Campus Box 4400, Normal, IL 61790-4400, USA.

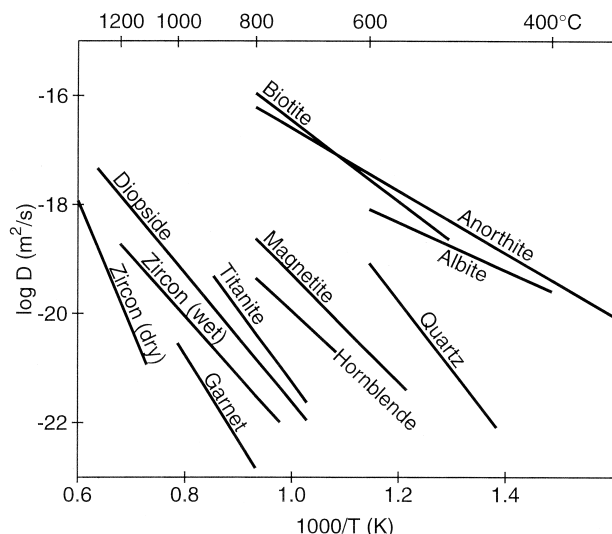


Fig. 1. Comparison of Arrhenius relations for oxygen diffusion in selected minerals under hydrothermal conditions at $\text{PH}_2\text{O} = 100$ MPa water pressure and anhydrous diffusion data for zircon (see text). Diffusion rates of oxygen in titanite and zircon are slower than in most common, granitic igneous minerals. The solid lines indicate the range of temperatures at which experiments were performed. Diffusion data: Garnet (Coghlan, 1990), Zircon (Watson and Cherniak, 1997), Titanite (Morishita et al., 1996), Diopside (Farver, 1989), Hornblende (Farver and Giletti, 1985), Magnetite (Giletti and Hess, 1988), Quartz (Farver and Yund, 1991), Albite (Elphick et al., 1986), Biotite (Fortier and Giletti, 1991), Anorthite (Giletti et al., 1978).

radius of $500 \mu\text{m}$ is 500°C (Farver and Yund, 1991). A zircon with an average radius of $100 \mu\text{m}$ has a closure temperature of approximately 600°C , using wet diffusion data with a cooling rate of $10^\circ\text{C}/\text{Ma}$ (Watson and Cherniak, 1997). Closure temperature for zircon under anhydrous conditions is $>800^\circ\text{C}$ for average zircon radii and cooling rates (Watson and Cherniak, 1997). Diffusion data indicate that titanite and zircon are the first two minerals in an average granitic rock to close to oxygen diffusion during cooling, and are similarly retentive of magmatic $\delta^{18}\text{O}$. The slow oxygen diffusion rates and high closure temperatures of titanite and zircon create ideal conditions for an empirical calibration of oxygen isotope fractionations.

Previously published fractionation factors for titanite were derived from the semiempirical, modified increment method:

$$1000 \ln \alpha(\text{Zrc} - \text{Ttn}) = 0.69 \times 10^6 / (\text{T}^2) \quad (\text{Hoffbauer et al., 1994})$$

$$1000 \ln \alpha(\text{Zrc} - \text{Ttn}) = (-0.05 \times 10^6 / \text{T}^2) - (0.15 \times 10^3 / \text{T}) + 0.07 \quad (\text{Zheng, 1993})$$

$1000 \ln \alpha(\text{A} - \text{B}) \approx \Delta_{\text{A-B}} = \delta^{18}\text{O}(\text{A}) - \delta^{18}\text{O}(\text{B})$ (Friedman and O'Neil, 1977) and temperature is in Kelvin. These equations result in Zrc-Ttn fractionations of 0.81‰ (Hoffbauer et al., 1994) and -0.15‰ (Zheng, 1993) at 650°C , a typical closure temperature of titanite to oxygen diffusion (Morishita et al., 1996). The large disagreement between the two modified increment method calibrations indicates that additional data are necessary to settle the discrepancy. We present empirical oxygen isotope fractionations for titanite with respect to zircon and

quartz based on analyses from felsic igneous and *meta*-igneous rocks of varied ages and metamorphic histories. Because titanite has slow oxygen diffusion and a high closure temperature, $^{18}\text{O}/^{16}\text{O}$ ratios should reflect the isotopic compositions preserved since crystallization, assuming the only subsolidus process affecting oxygen is volume diffusion. The $\delta^{18}\text{O}$ of titanite can be used to distinguish igneous vs. metamorphic or hydrothermal assemblages. We will also formulate a quartz-titanite fractionation factor and test it for self-consistency with measured values.

2. SAMPLE DESCRIPTIONS AND TECHNIQUES

Forty seven titanite-bearing samples were analyzed from a wide variety of geological environments (Table 1). Sixteen samples are from Archean granitoids of the Superior Province, Canada and Barberton Mountain Land, South Africa. Locations of Superior Province samples are given by King et al. (1998). Barberton Mountain Land sample locations are given by Kamo and Davis (1994). The titanite and zircon from these samples have been dated using U-Pb geochronology techniques (see Table 1). Eleven of the Archean samples contain igneous titanite and igneous zircon, while five Archean samples contain metamorphic titanite and igneous zircon. The igneous titanite U-Pb ages are, on average, within 0.8 m.y. of the zircon age and the titanite has a high average Th/U ratio of 4.66. In contrast, the metamorphic titanites have U-Pb ages more than 5 m.y. younger than zircon, with ages ranging from 6 to 49 m.y. younger than zircon, and an average Th/U ratio of 1.15. The highest grade of metamorphism the Archean samples have experienced is greenschist facies. Not all samples that experienced regional metamorphism crystallized metamorphic titanite, as shown by U-Pb geochronology.

Thirty one titanite-bearing samples are from Phanerozoic granitoids of the Idaho batholith and northern Great Basin. Locations of Idaho batholith samples are in King and Valley (2001). Great Basin sample locations are described in Kowallis (1990), Sullivan (1991), and King (2001). The titanite in Phanerozoic samples from the western United States is assumed to be igneous. The country rocks indicate that regional metamorphic temperatures did not exceed 500°C after emplacement of the plutons. Since the blocking temperatures of titanite and zircon were not attained during any metamorphic event in these samples, the quenched magmatic $\delta^{18}\text{O}$ should be preserved.

Mineral separates were prepared at the Royal Ontario Museum, University of Wisconsin, and Brigham Young University. Zircons were separated from 15 to 20 kg samples using standard crushing, hydraulic, magnetic and heavy liquid techniques. The Frantz magnetic separator was set at 1.7 Amps, 10° forward tilt, and side tilts from 0° to 4° . Zircon was cleaned in hydrofluoric acid. The least magnetic fraction of zircon available was analyzed to limit complications related to alteration that is occasionally associated with magnetic zircons (Krogh, 1982; Valley et al., 1994). Samples approximately 0.5 kg were crushed and sieved to separate titanite and quartz. All minerals were handpicked under a binocular microscope. Quartz was cleaned in hydrofluoric and hydrochloric acid, to confirm purity, and then repicked and judged to be $>99\%$ pure.

Oxygen isotope ratios of 1 to 2 mg mineral separates were analyzed at the University of Wisconsin by laser fluorination, in

Table 1. Oxygen isotope ratios of titanite, zircon and quartz for felsic igneous rocks.

Sample Number	Igneous Titanite $\delta^{18}\text{O}$ ‰	Zircon $\delta^{18}\text{O}$ ‰*	Quartz $\delta^{18}\text{O}$ ‰	Metamorphic Titanite		$\Delta(\text{Zrc-Ttn})$	$\Delta(\text{Qtz-Ttn})$	Zircon U-Pb age	Titanite U-Pb age	Titanite-Zircon		Titanite Th/U	Igneous body
				$\delta^{18}\text{O}$ ‰	Age Difference					Age Difference			
Archean samples													
Igneous titanite, Superior Province													
K76-2 ^a	5.88 ± 0.06	6.63 ± 0.14			0.75			2679	2679	0		8.76	Otto Stock syenite
DD81-12 ^a	4.95 ± 0.07	6.27 NM1, M0	10.27 ± 0.02		1.32	5.32		2686.1	2683.2	2.9		6.66	Ottertail stock quartz monzonite
DD81-29 ^a	4.59 ± 0.01	5.94 ± 0.08 NM0	7.98 ± 0.06		1.35	3.39		2701	2699.2	1.8		1.89	Herony diorite
DD87-51 ^a	4.13 ± 0.02	5.58 NM1			1.45			2695	2695	0		4.77	Sandybeach Lake stock
C92-20 ^a	5.22 ± 0.01	6.30 ± 0.04 M0	9.44 ± 0.20		1.08	4.22		2681	2681	0		6.8	Perching Gull Lake quartz-monzonite
C86-14 ^a	5.21 ± 0.05	6.53 ± 0.03 M0			1.32			2678	2678	0		5.55	Gowan Lake pluton quartz-monzonite
C92-30 ^a	4.57 ± 0.08	7.08 ± 0.05 M0			1.21			2690	2690	0		2	Saganaga tonalite, Shebandowan
C82-18 ^a	5.68 ± 0.20	7.03 ± 0.16 NM0			1.35			2668	2664	4		0.95	Mongoose Lake monzonite, Batchawana
C88-23 ^a	4.98 ± 0.04	6.35 ± 0.03 M0			1.37			2700	2700	0		5.67	Graniteboss stock granodiorite
Igneous titanite, Barberton Mountain Land													
B87-25 ^b	5.14 ± 0.03	6.00 ± 0.19	9.96 ± 0.02		0.86	4.82		3107	3107	0		3.1	Mpuluzi batholith
B87-20 ^b	5.52 ± 0.02	6.55 ± 0.03	9.47		1.03	3.95		3107	3107	0		5.15	Boesmanskop pluton
Metamorphic titanite, Superior Province													
DD84-19 ^a		6.13 NM0, M0			3.78 ± 0.06			2727	2703	24		0.78	High Lake stock late granodioritic phase
DD81-30 ^a		5.69 ± 0.06 NM0			3.05 ± 0.07			2723.2	2674	49.2		0.73	Sabaskong batholith tonalite gneiss
DD81-17 ^a		5.42 ± 0.14 NM0			3.82 ± 0.01			2716.8	2693.4	23.4		0.34	Aulneau batholith, early to nalitic phase
C82-17 ^a		7.52 M0			5.45 ± 0.04			2668	2662	6		1.22	Mongoose Lake hornblende, Batchawana
DD81-16 ^a		6.28 NM0			4.56 ± 0.08			2709.7	2696.3	13.4		2.66	Aulneau batholith, late granodioritic phase
Phanerozoic samples													
Northern Great Basin													
Bull-1 ^c	4.66 ± 0.09	5.36 ± 0.15			0.70								Bull Mountain
HIL-10 ^f	5.10 ± 0.04	6.49 ± 0.11			1.39								Henry Mountains
HIL-1 ^c	5.08 ± 0.04	5.95 ± 0.09			0.87								Henry Mountains
FC7	4.75	5.61 ± 0.04			0.86								Fish Canyon Tuff
LC-9 ^d	4.65 ± 0.06	6.01		1.36									Little Cottonwood stock
LC-2 ^d	4.02 ± 0.06	5.26 ± 0.04		1.24									Little Cottonwood stock
LC-5 ^d	4.24 ± 0.04	5.82 ± 0.01			1.58								Little Cottonwood stock
LC-15 ^d	5.21 ± 0.07	6.14 ± 0.01			0.93								Little Cottonwood stock
LC-33 ^d	4.79 ± 0.01	5.96			1.17								Little Cottonwood stock
LC-34 ^d	4.78 ± 0.01	6.01			1.23								Little Cottonwood stock
NP-1	6.37 ± 0.18	7.22 ± 0.18	10.45 ± 0.12		0.85	4.53							Notch Peak pluton, Utah
99GB-30	5.92 ± 0.00												Crater Island South Stock,
99GB-27	5.90 ± 0.11		10.59 ± 0.28			4.69							Silver Island Range Utah
99GB-28	5.83 ± 0.01		10.60 ± 0.01			4.77							Crater Island South Stock,
99GB-54	5.89		10.42 ± 0.09			4.53							Silver Island Range Utah
99GB-56	6.40 ± 0.09		10.72 ± 0.09			4.32							Dolly Varden Mountains,
99GB-34	6.22		9.86 ± 0.01			3.64							Melrose pluton, Utah
99GB-99	4.94 ± 0.05		9.88 ± 0.02			4.94							Dolly Varden Mountains,
													Melrose pluton, Utah
													Dolly Varden Mountains,
													Melrose pluton, Utah
													Imigrant Pass/Grouse
													Creek Mountains, Utah
													Granite Range, Nevada

Table 1. (Continued)

Sample Number	Igneous		Metamorphic		$\Delta(\text{Zrc-Tm})$	$\Delta(\text{Qtz-Tm})$	Zircon U-Pb age	Titanite U-Pb age	Titanite-Zircon Age Difference	Titanite Th/U	Igneous body
	Titanite $\delta^{18}\text{O}$ ‰	Zircon $\delta^{18}\text{O}$ ‰*	Quartz $\delta^{18}\text{O}$ ‰	Titanite $\delta^{18}\text{O}$ ‰							
99GB-96	4.86 ± 0.09		9.88 ± 0.22			5.02					Granite Range, Nevada
99GB-130	7.18 ± 0.11		11.67 ± 0.06			4.49					Austin pluton, Toiyabe Range, Nevada
99GB-87	6.89 ± 0.08		11.42 ± 0.31			4.53					Osgood Mountains, Nevada
99GB-104	5.1 ± 0.05		9.49 ± 0.03			4.39					Prison Hill, Nevada
Idaho Batholith ^e											
98IB-61	5.52 ± 0.05	7.34 ± 0.12 NM4	10.23 ± 0.05		1.82	4.71					Twin Springs pluton, Idaho batholith
98IB-53	5.46 ± 0.04	6.66 ± 0.07 NM4	10.67 ± 0.11		1.2	5.21					Atlanta lobe, Idaho batholith
98IB-39	6.62 ± 0.14	7.67 ± 0.03 NM2	11.04 ± 0.35		1.05	4.42					Atlanta lobe, Idaho batholith
98IB-34	6.38 ± 0.09	7.75 ± 0.11 NM2	10.70 ± 0.00		1.37	4.32					Atlanta lobe, Idaho batholith
98IB-52	6.73 ± 0.08	7.99 ± 0.05 NM1	11.25 ± 0.03		1.26	4.52					Atlanta lobe, Idaho batholith
98IB-51	6.68 ± 0.01		11.27			4.59					Atlanta lobe, Idaho batholith
98IB-49	6.38 ± 0.05		11.05 ± 0.13			4.67					Atlanta lobe, Idaho batholith
98IB-35	6.49 ± 0.12		11.06 ± 0.18			4.57					Atlanta lobe, Idaho batholith
98IB-10	6.43 ± 0.05		10.87 ± 0.09			4.44					Bitterroot lobe, Idaho batholith

* : NM0, M0, NM1, NM2, NM4 designate the magnetic susceptibility (magnetic or nonmagnetic) and the side tilt (in degrees) at 1.7 amps and 10° forward tilt of the Frantz magnetic separator.

^a : see King et al., 1998 for sample locations and geochronology references.

^b : see Kamo and Davis, 1994 for sample locations and geochronology.

^c : see Sullivan et al., 1991 for sample locations.

^d : see Kowallis et al., 1990 for sample locations.

^e : see King and Valley, in press for sample locations.

the presence of BrF_5 , and mass spectrometry (Valley et al., 1995). The oxygen isotope ratios are reported in standard δ -notation (‰) relative to Vienna Standard Mean Ocean Water (V-SMOW). Zircon grains from Phanerozoic samples were analyzed after powdering in a boron carbide mortar and pestle to avoid any possible grain size effects during analyses and to maximize the yield of oxygen. Quartz grains were analyzed using rapid heating and a defocused laser beam (Spicuzza et al., 1998).

The analytical precision for $\delta^{18}\text{O}$ in this study is ± 0.06 (1 sd, 1 se = 0.005‰) for 144 aliquots of UWG-2 garnet standard that were analyzed on 38 days concurrently with the mineral separates. On several days, daily averages of UWG-2 were lower or higher (0.03–0.22‰) than the accepted value of 5.80‰ (relative to 9.59‰ for NBS-28). Analyses of unknown samples from these days have been corrected by this small amount as recommended by Valley et al. (1995). The average correction was 0.09‰. The average reproducibility of duplicated titanite, zircon, and quartz analyses is ± 0.06 ‰ ($n = 44$), ± 0.08 ‰ ($n = 24$), and ± 0.11 ‰ ($n = 23$) respectively.

3. RESULTS

3.1. Diffusion

Calculations of oxygen diffusion distances in titanite and zircon (Eqn. 2.45 Crank, 1975), using diffusion data of Morishita et al. (1996) and Watson and Cherniak (1997), show that diffusion during 10 m.y. at a constant temperature of 400°C or 500°C (a reasonable duration and upper temperature limit of greenschist metamorphism, the highest grade of metamorphism samples in this study have experienced) is not a significant process. The diffusion distance in a titanite crystal (for 50% exchange) for 10 m.y. is 0.3 μm at 400°C and 4.6 μm at 500°C. These diffusion distances represent 0.3% and 5.2 volume% of an average titanite crystal (1000 $\mu\text{m} \times 750 \mu\text{m} \times 300 \mu\text{m}$). The diffusion distance in zircon (for 50% exchange) under hydrous conditions for 10 m.y. is 0.3 μm at 400°C and 3.3 μm at 500°C. These diffusion distances represent 0.7% and 7.5 volume% of an average zircon grain (300 $\mu\text{m} \times 100 \mu\text{m} \times 100 \mu\text{m}$). For comparison, the diffusion distances in quartz under hydrothermal conditions for 10 m.y. are 36 μm at 400°C and 590 μm at 500°C. The diffusion distance in zircon (for 50% exchange) under dry conditions for 10 m.y. is $8.2 \times 10^{-7} \mu\text{m}$ at 400°C and $1.5 \times 10^{-4} \mu\text{m}$ at 500°C. These distances are less than 0.001 volume% of a zircon grain that is 300 $\mu\text{m} \times 100 \mu\text{m} \times 100 \mu\text{m}$. These calculations indicate that diffusive exchange in titanite and zircon will not significantly affect the $\delta^{18}\text{O}$ of these minerals due to the extremely small diffusion distances at these temperatures and durations, assuming diffusion is the only effective subsolidus process.

The extent of $\delta^{18}\text{O}$ alteration in titanite and zircon due to diffusion can be quantified by calculating the percent exchange of oxygen at various temperatures and durations. Oxygen exchange in 1 volume% and 10 volume% (for 50% exchange) of titanite and zircon grains, with idealized spherical crystal diameters of 400 μm and 200 μm , respectively, is plotted in Figure 2. Less time is needed to exchange oxygen in 1 and 10% of each grain with increased temperature of metamorphism. Titanite and zircon crystals can endure greenschist facies metamorphism, under hydrothermal conditions, for approximately

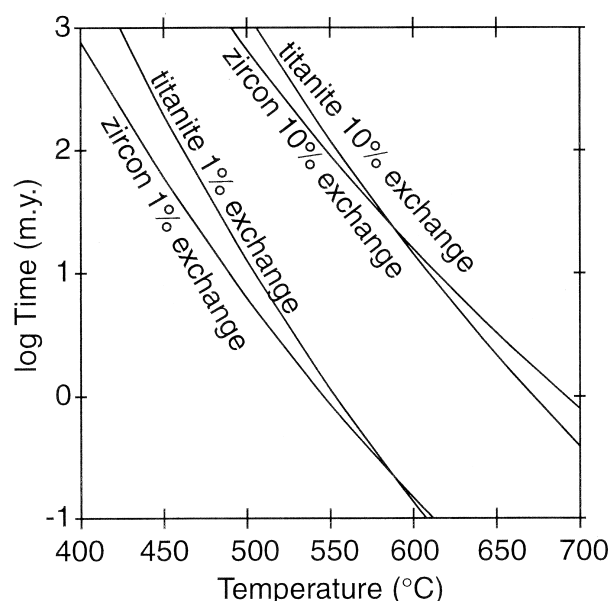


Fig. 2. Plot of temperature vs. log time for diffusional exchange of oxygen in titanite and zircon with an external reservoir. 1 and 10 volume% exchange (50% isotopic shift) are based on the volume of an idealized 200 μm diameter spherical zircon and 400 μm spherical titanite crystal, oxygen diffusion rates under hydrothermal conditions, and variable diffusion rates with temperature. Titanite and zircon crystals can endure greenschist facies metamorphic conditions for approximately 10 m.y. before more than 1% of the grain exchanges oxygen.

10 m.y. before greater than 1% of the grain exchanges oxygen. This metamorphic temperature and duration is a maximum estimate for metamorphism experienced by samples in this study.

3.2. Mineral Fractionations

Oxygen isotope ratios of titanite, zircon and quartz are reported in Table 1 and on Figures 3–5. The average $\Delta(\text{Zrc-Ttn})$ is 1.18 ± 0.27 ‰ for all igneous titanite samples (Fig. 3). The average $\Delta(\text{Zrc-Ttn})$ of the Archean samples with igneous titanite is 1.19 ± 0.23 ‰ ($n = 11$ rocks). The average $\Delta(\text{Zrc-Ttn})$ of the Phanerozoic samples is 1.18 ± 0.30 ‰ ($n = 16$ rocks). The average fractionation of metamorphic titanite and igneous zircon is 2.08 ± 0.43 ‰ ($n = 5$ rocks), which differs significantly from the igneous titanite-zircon average fractionation (Fig. 4).

There is more variation between the quartz-titanite fractionations of the Archean and Phanerozoic samples than observed in zircon-titanite fractionations of the two ages. The average $\Delta(\text{Qtz-Ttn})$ of all samples is 4.52 ± 0.43 (Fig. 5). The average $\Delta(\text{Qtz-Ttn})$ of Archean samples is 4.34 ± 0.75 ‰ ($n = 5$ rocks). Phanerozoic samples have an average $\Delta(\text{Qtz-Ttn}) = 4.57 \pm 0.32$ ‰ ($n = 20$ rocks). The deviation of the average fractionation for Archean samples from the Phanerozoic samples may be due to subsolidus exchange in quartz during the greenschist facies metamorphism that Archean samples experienced (King et al., 1998).

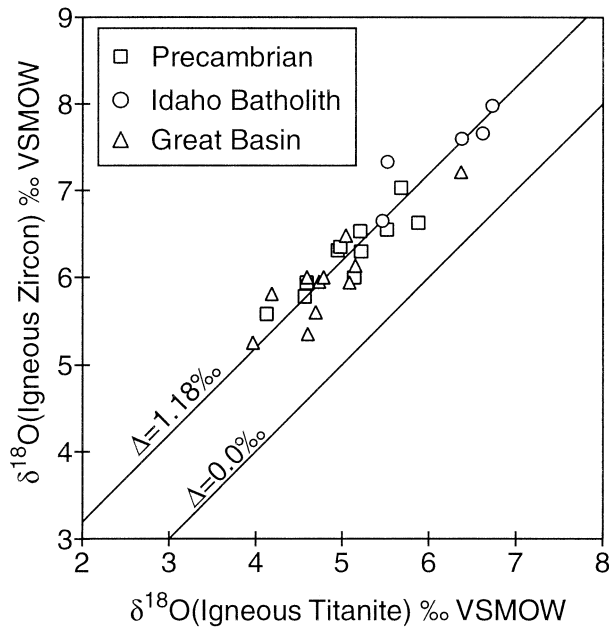


Fig. 3. Plot of $\delta^{18}\text{O}$ (igneous titanite) versus $\delta^{18}\text{O}$ (igneous zircon) for Precambrian samples from the Superior Province and Barberton Mountain Land and Phanerozoic samples from the Idaho batholith and northern Great Basin. The average measured zircon-titanite fractionation is $1.18 \pm 0.2\%$ ($n = 27$ rocks). The igneous nature of Precambrian titanite and zircon was determined by U-Pb geochronology (see Table 1). Phanerozoic titanite is assumed to be igneous due to the lack of regional metamorphism.

4. INTERPRETATION AND DISCUSSION

4.1. Zircon-Titanite Fractionation Factor

A $1/T^2$ dependence (T in Kelvin) is assumed for isotope fractionations with the following equation:

$$\Delta(\text{mineral}_B - \text{mineral}_C) = (A_{\text{mineral}_B - \text{mineral}_C} \times 10^6) / T^2$$

where A is a constant called the "A-factor." The average measured $\Delta(\text{Zrc-Ttn}) = 1.2\%$ for igneous titanite and zircon and an assumed temperature of 650°C (the closure temperature of a $500 \mu\text{m}$ diameter titanite crystal to oxygen diffusion with a cooling rate of $10^\circ\text{C}/\text{Ma}$) results in the following equation fitting a straight line to the data through the origin on a fractionation vs. $1/T^2$ plot:

$$\Delta(\text{Zrc} - \text{Ttn}) = 1.02 \times 10^6 / (T^2)$$

The A-factor is not overly sensitive to changes in cooling rate or grain size. If the cooling rate is $20^\circ\text{C}/\text{Ma}$ for a titanite grain measuring $500 \mu\text{m}$, the closure temperature is 673°C , resulting in an A-factor of 1.07. A cooling rate of $10^\circ\text{C}/\text{Ma}$ and grain size of $1000 \mu\text{m}$ results in a closure temperature of 693°C and an A-factor of 1.12.

The equation based on data from this study predicts larger fractionations between titanite and zircon than the two fractionation factors from the increment method (Fig. 6). The negative $\Delta(\text{Zircon-Titanite})$ predicted by Zheng (1993) is not observed in natural samples. The fractionations predicted by Hoffbauer et al. (1994) are closer to, but significantly smaller than, the

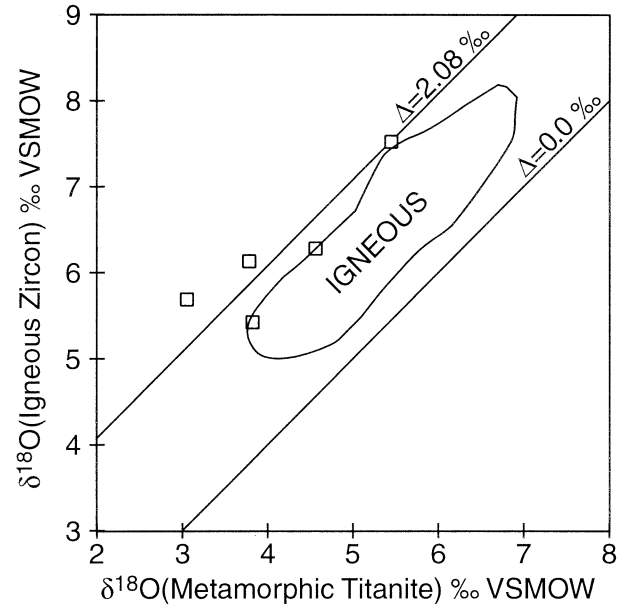


Fig. 4. Plot of $\delta^{18}\text{O}$ (metamorphic titanite) versus $\delta^{18}\text{O}$ (igneous zircon) from the Superior Province. The average measured fractionation is 2.08 ± 0.43 ($n = 5$ rocks). The ages of titanite and zircon was determined by U-Pb geochronology (see Table 1). The field of igneous zircons vs. igneous titanite (Fig. 3) is shown for comparison.

measured $\Delta(\text{Zircon-Titanite})$. The observed average fractionation results in an apparent temperature of 485°C , using the Hoffbauer et al. (1994) A-factor of 0.69. This temperature is well below the closure temperature of both titanite and zircon, and not representative of any geologic event.

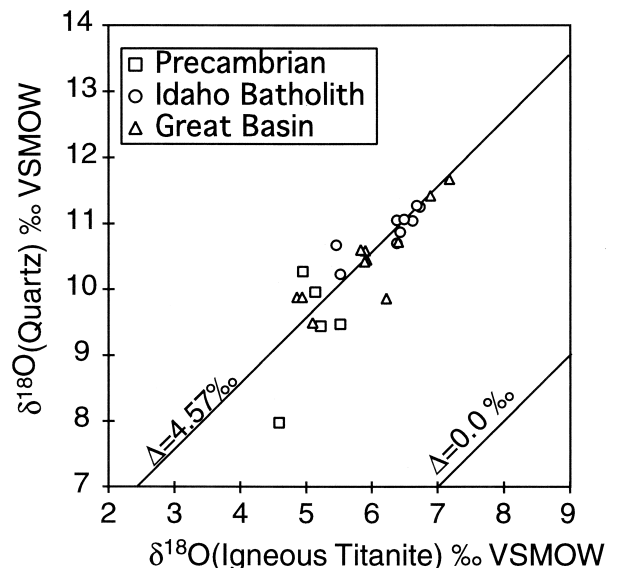


Fig. 5. Plot of $\delta^{18}\text{O}$ (igneous titanite) versus $\delta^{18}\text{O}$ (quartz) from the Superior Province, Barberton Mountain Land, Idaho batholith, and northern Great Basin. The average measured fractionation is $4.57 \pm 0.32\%$ ($n = 20$ rocks). The Precambrian quartz $\delta^{18}\text{O}$ values are reset by subsolidus exchange.

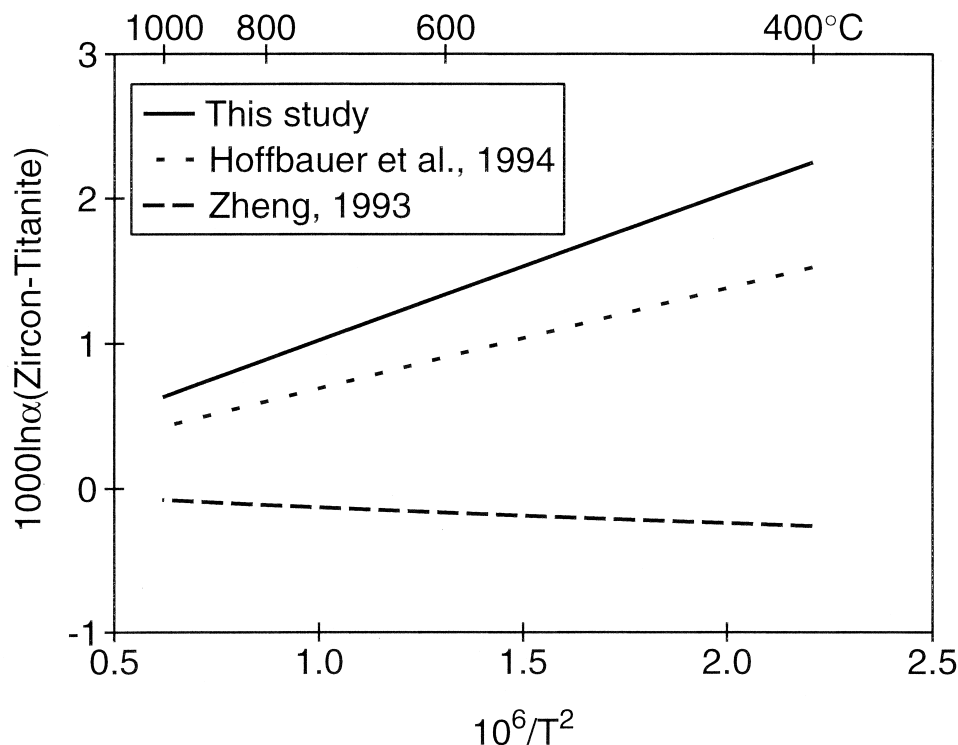


Fig. 6. Comparison of oxygen isotope fractionation factors between zircon and titanite from this study and two increment method fractionations vs. $10^6/T^2$.

4.2. Quartz-Titanite Fractionation Factor

The fractionation factor for quartz-titanite is obtained by combining our zircon-titanite A-factor with previously published experimental and empirical A-factors.

$1000 \ln \alpha(\text{Quartz-Diopside}) = 2.75 \times 10^6/(T^2)$ (Chiba et al., 1989)

$1000 \ln \alpha(\text{Diopside-Almandine}) = -0.20 \times 10^6/(T^2)$ (Kohn and Valley, 1998a)

$1000 \ln \alpha(\text{Almandine-Zircon}) = 0.0$ (Valley et al., 1994)

$1000 \ln \alpha(\text{Zircon-Titanite}) = 1.02 \times 10^6/(T^2)$ (this study)

$1000 \ln \alpha(\text{Quartz-Titanite}) = 3.57 \times 10^6/(T^2)$

This equation is in contrast to the increment method equations of

$1000 \ln \alpha(\text{Quartz-Titanite}) = 2.75 \times 10^6/(T^2)$ (Hoffbauer et al., 1994)

$1000 \ln \alpha(\text{Quartz-Titanite}) = (0.67 \times 10^6/T^2) + (4.11 \times 10^3/T) - 1.72$ (Zheng, 1993)

The fractionation factor from this study results in an apparent temperature of 610°C for the average $\Delta(\text{Qtz-Ttn})$ of Phanerozoic samples in this study. Applying the increment method equations to the average quartz-titanite fractionation of the Phanerozoic samples results in apparent temperatures of 502°C (Hoffbauer et al., 1994) and 515°C (Zheng, 1993). The data from this study predict a larger $\Delta(\text{Qtz-Ttn})$ at any temperature than the increment method (Fig. 7).

4.3. Comparison of Diffusion Model Results with Empirical Data

To test the validity of the quartz-titanite A-factor of this study in comparison to A-factors from the increment method, the cooling of an average granite was simulated with the Fast Grain Boundary (FGB) diffusion model of Eiler et al. (1992; 1994) with small modifications by Kohn and Valley (1998b). FGB calculations predict mineral fractionations due to diffusion for different rates of cooling, diffusion rates, mineral sizes and modes, and fractionation factors. Cooling rates of 10°C/m.y. to 60°C/m.y. were assumed. Only minerals with >1% mode were included in the FGB diffusion model and diffusion rates for hydrothermal conditions were used for all minerals (Table 2). Grain size and modes, fractionations and diffusion parameters for the calculations are average values for the samples studied. Quartz-titanite fractionation factors from this study, Zheng (1993), and Hoffbauer (1994) were used for comparison purposes with measured $\Delta(\text{Qtz-Ttn})$ (Table 2).

The FGB model, using the quartz-titanite A-factor from this study, predicts $\Delta(\text{Qtz-Ttn}) = 4.56\text{‰}$ to 4.16‰ for cooling rates between 10°C/m.y. and 60°C/m.y. (Fig. 8). The predicted $\Delta(\text{Qtz-Ttn})$ using the Qtz-Ttn A-factor of Hoffbauer et al. (1994), for the same cooling rates, is 3.63‰ to 3.33‰. The FGB model, using the quartz-titanite fractionation A-factor of Zheng (1993) for the same range of cooling rates predicts a $\Delta(\text{Qtz-Ttn}) = 3.93\text{‰}$ to 3.62‰. Figure 8 shows that the data from coexisting quartz-titanite pairs best fits the FGB model

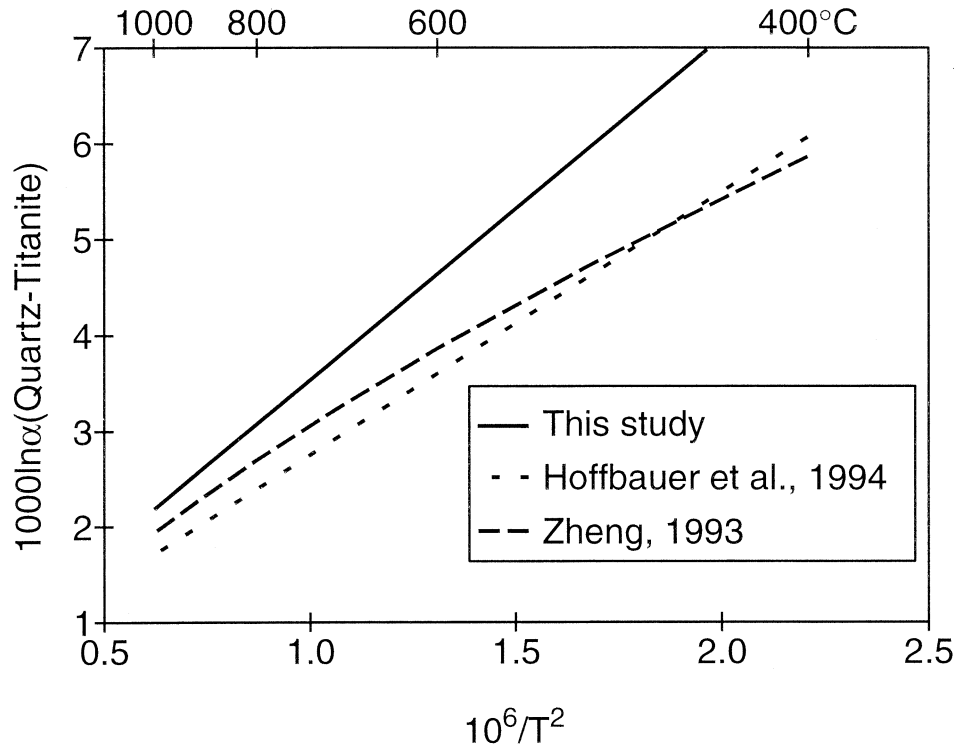


Fig. 7. Comparison of oxygen isotope fractionation factors between quartz and titanite from this study and two increment method fractionations vs. $10^6/T^2$.

results using the quartz-titanite A-factor derived from this study. The average measured $\Delta(\text{Qtz-Ttn}) = 4.52 \pm 0.43\text{‰}$. Modeling of oxygen exchange during cooling using the incre-

ment method A-factors results in fractionations much smaller than those measured.

4.4. Titanite as an Indicator of Magmatic $\delta^{18}\text{O}$

The average measured $\Delta(\text{Zrc-Ttn})$ and $\Delta(\text{Qtz-Ttn})$ of this study are similar to the limited published titanite data. Coexisting zircon and titanite $\delta^{18}\text{O}$ analyses from Proterozoic granitic rocks in Sweden are reported with an average $\Delta(\text{Zrc-Ttn})$ of $1.25 \pm 0.35\text{‰}$ (Munksgaard and Zeck, 1984; Munksgaard and Zeck, 1985). The average $\Delta(\text{Qtz-Ttn})$ of these Proterozoic granitoids is larger (5.37 ± 0.38) than the $\Delta(\text{Qtz-Ttn})$ of this study, probably due to hydrothermal alteration of the rocks that is described by Munksgaard and Zeck (1984). Quartz-titanite fractionations in unaltered, plutonic rocks from Transbaikalia, East Asia have an average $\Delta(\text{Qtz-Ttn}) = 4.4\text{‰}$ ($n = 18$) (Wickham et al., 1996), which is slightly reset from igneous fractionations as shown by the data of this study. Titanite $\delta^{18}\text{O}$ data from Transbaikalia have also been used to “see through” hydrothermal alteration events to provide information of magmatic source (Wickham et al., 1996). The trend of decreasing titanite $\delta^{18}\text{O}$ over nearly 250 m.y. of intrusion events is tighter and more apparent than the trend of quartz $\delta^{18}\text{O}$ through time. Zircon $\delta^{18}\text{O}$ data are needed to definitively evaluate the titanite $\delta^{18}\text{O}$ data, but igneous titanite could potentially be an important tool to determine magmatic $\delta^{18}\text{O}$ in altered rocks.

4.5. Titanite as a Thermometer

With a well calibrated A-factor, titanite is a potentially useful mineral for thermometry, especially in carbonate rocks or

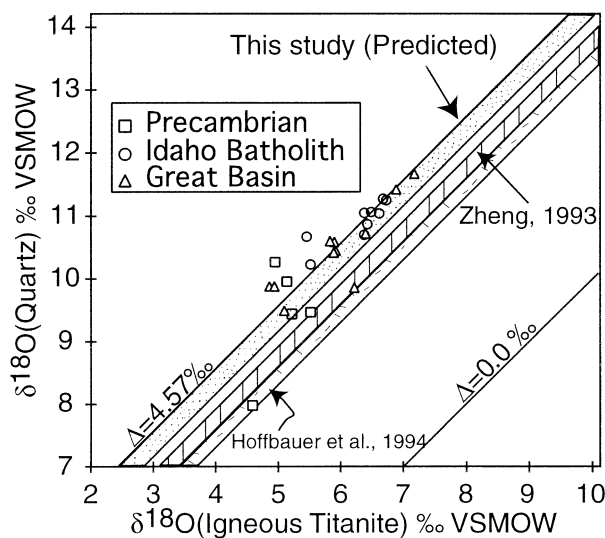


Fig. 8. Plot of $\delta^{18}\text{O}(\text{igneous Ttn})$ versus $\delta^{18}\text{O}(\text{Qtz})$ from the Superior Province, Barberton Mountain Land, Idaho batholith, and northern Great Basin with the fields of the predicted fractionation from the Fast Grain Boundary diffusion model using the $\Delta(\text{Qtz-Ttn})$ from this study, Hoffbauer et al. (1994), and Zheng (1993). The A-factor from this study, based on the combination of the measured titanite-zircon fractionation from this study and other published experimental and empirical fractionations, best fits the data.

Table 2. Oxygen diffusion rates and fractionation factors used in Fast Grain Boundary (FGB) modelling.

Mineral	Q	D ₀	Reference	A	Reference
Quartz	243	2.90E-05	Farver and Yund (1991)	0	—
Plagioclase (An ₂₀)	85	1.00E-13	Elphick et al. (1986)	1.20	Clayton et al. (1989)
K-feldspar	85	1.00E-13	Elphick et al. (1986)	1.00	Clayton et al. (1989)
Biotite	142	9.10E-10	Fortier and Giletti (1991)	2.16	Chacko et al. (1996)
Titanite	254	1.00E-08	Morishita et al. (1996)	3.57	This study
				2.75	Hoffbauer et al. (1994)
				0.67	Zheng (1996)
Magnetite	188	3.50E-10	Giletti and Hess (1988)	6.29	Chiba et al. (1989)

Note: D_0 (pre-exponential factor in m^2s^{-1}) and Q (Activation energy in kJ mol^{-1}) are from the Arrhenius relationship for the diffusion coefficient: $D = D_0 \exp(-Q/RT)$ where R is the gas constant and T is temperature (K). A-factors are for the formula $\Delta(\text{Qtz-Mineral}) = A \times 10^6/T^2$. Granitoid is modeled as 30% quartz, 40% plagioclase, 20% K-feldspar, 8% biotite, 1% titanite, 1% magnetite.

quartzites. To test our calibration, calcite-graphite carbon isotope thermometry from previously published data was compared with calcite-titanite oxygen isotope thermometry. The combination of the quartz-titanite A-factor from this study with the previously published calcite-quartz A-factor (Sharp and Kirschner, 1994) results in the Eqn. $1000 \ln \alpha(\text{Calcite-Titanite}) = 2.70 \times 10^6/(T^2)$ (but see Clayton et al., 1989). Hoffbauer and Spiering (1994) report oxygen isotope data from calcite and titanite along with carbon isotope data from calcite and graphite from granulite facies rocks in Sri Lanka. Carbon isotope calcite-graphite temperatures calculated with the Kitchen and Valley (1995) calibration and oxygen isotope temperatures calculated with the calcite-titanite A-factor of this study are nearly identical (Table 3) for samples with primary calcite, graphite and titanite. Samples BSL9/1 and BSL22/2, as reported in Hoffbauer and Spiering (1994), contain secondary calcite, so thermometry is not representative of equilibrium temperatures and they are not listed in Table 3. In all four samples with primary calcite, the largest temperature discrepancy between carbon and oxygen isotope data is 61°C. This

small difference can be accounted for by variability of 0.3‰ in the oxygen isotope analyses.

Additional oxygen isotope thermometry confirms the calcite-graphite and calcite-titanite thermometry. The average measured fractionation between diopside and titanite in granulite facies rocks from Sri Lanka is 0.82‰ (Hoffbauer and Spiering, 1994). Oxygen isotope diopside-titanite temperatures calculated with the Chiba et al. (1989) diopside-quartz calibration and the quartz-titanite calibration of this study results in a temperature of 715°C. This temperature differs by less than 40° from the average temperatures calculated with calcite-graphite and calcite-titanite thermometry. A variability of 0.1‰ in the oxygen isotope analyses accounts for the difference in temperatures.

Calcite-titanite thermometry from granulite and upper amphibolite facies marbles of the Adirondack Mountains, New York does not consistently agree with calcite-graphite thermometry. This discrepancy is not due to error in the calibration, but indicates open system fluid infiltration of an oxygen-rich fluid that preferentially exchanged oxygen isotopes with the

Table 3. Stable isotope data and thermometry from titanite-bearing carbonate rocks.

Sample	$\Delta^{13}\text{C}(\text{Cc-Gr})$	$\Delta^{18}\text{O}(\text{Cc-Ttn})$	$T^\circ\text{C}(\text{Cc-Gr})^a$	$T^\circ\text{C}(\text{Cc-Ttn})^b$	$^{18}\text{O } T - ^{13}\text{C } T$ (°C)
Granulite Facies					
Sri Lanka					
(Hoffbauer and Spiering 1994)					
SL 107/1	4.3	3.0	637	676	39
BSL 39/1	3.6	3.1	721	660	-61
BSL 39/4	4.1	3.2	659	646	-13
BSL 44/2	3.8	2.7	695	727	32
Granulite and Upper Amphibolite Facies					
Adirondack Mts					
(Kitchen and Valley, 1995)					
NC8 [‡]	3.29	2.83	767	704	-63
BL 3-1	3.19	2.9	783	692	-92
IL13	3.47	3.57	740	597	-143
LP 8-2	2.9	-4.07	835	NA	NA
TP 10-1	3.31	3.6	764	593	-171
NC 12	3.23	3.93	777	556	-221
SL5-2	3.47	3.42	740	616	-124
93NK-1	3.35	2.78	758	713	-45
GOV 100	3.8	3	695	676	-19
93NK3	4.01	3.38	669	621	-48
92FC6	4.1	1.96	659	901	242

[‡] Calcite and graphite data from Kitchen and Valley, (1995). Titanite data this study. ^a: calibration of Kitchen and Valley, (1995).

^b: calibration of this study.

rock and did not alter carbon isotopes. Kitchen and Valley (1995) document calcite recrystallization that had limited influence on the carbon isotope thermometry. Due to the sensitivity of the calcite-titanite thermometer, if $\delta^{18}\text{O}$ calcite had been reset by 0.5‰, then the apparent temperature is reset by 100°C. An arkosic quartzite (sample Cq of Corfu and Easton (1997)) from the Frontenac Terrane of the Grenville Province has $\delta^{18}\text{O}(\text{Qtz})$ of 22.96‰ and $\delta^{18}\text{O}(\text{Ttn})$ of 19.20‰, resulting in a temperature of 701°C. Other temperature estimates for this region are 700 to 750°C (Anovitz and Essene, 1990; Streepey et al., 1997) which is in good agreement with our quartz-titanite temperature.

Stable isotope thermometry in metamorphic rocks is dependent on the mineral closure temperature being higher than the peak of metamorphism. The closure temperature of titanite with a typical upper crustal cooling rate of 10°C/m.y. is 650°C. A typical cooling rate for the Adirondack granulite facies rocks (1°C/m.y.) results in the titanite closure temperature at 600°C. The temperatures of granulite facies metamorphism are above these closure temperatures, but these temperatures are for hydrous conditions. The lack of diffusion data for titanite under anhydrous conditions limits the use of this mineral as a thermometer, but diffusion rates will likely be slower and the closure temperature will be higher than those calculated under hydrous conditions (Farver and Yund, 1991; Watson and Cherniak, 1997).

5. CONCLUSIONS

Apparent temperatures resulting from calculations using A-factors for titanite derived from the semiempirical increment method are not consistent with independent thermometry. Such apparent temperatures are well below the temperature at which diffusion calculations predict exchange of oxygen to effectively cease. Our new calibration of the zircon-titanite A-factor derived from empirical measurements, with known U-Pb ages to confirm the igneous nature of the titanite, results in the Eqn. $1000\ln\alpha(\text{Zircon-Titanite}) = 1.02 \times 10^6/(T^2)$. This value, in combination with other published values, results in: $1000\ln\alpha(\text{Qtz-Ttn}) = 3.57 \times 10^6/(T^2)$. The FGB diffusion model of minerals in an average granitic rock exchanging oxygen during a range of geologic cooling rates indicates that the A-factor for $\Delta(\text{Qtz-Ttn})$ from this study best describes the measured data from coexisting quartz and titanite. The increment method studies result in $\Delta(\text{Qtz-Ttn})$ smaller than observed in nature. These empirical results based on titanite and zircon data yield self-consistent predictions of equilibrium fractionation between other minerals.

Acknowledgments—We thank M.J. Spicuzza for assistance in the stable isotope lab, F. Corfu and T.E. Krogh for discussion and access to the collection at the Royal Ontario Museum. We thank D.J. Cherniak, S. Hoernes, R. Hoffbauer, K. Mezger, W.H. Peck, and an anonymous reviewer for comments on this manuscript. This research was supported by NSF: EAR-96-28260 and EAR-99-02973, DOE: FG02-93ER14389, and a Dean Morgridge Wisconsin Distinguished Graduate Fellowship (to EMK). Field work was supported by University of Wisconsin Department of Geology.

Associate editor: K. Mezger

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