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Empirical calibration of oxygen isotope fractionation in zircon

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Abstract—New empirical calibrations for the fractionation of oxygen isotopes among zircon, almandine-rich garnet, titanite, and quartz are combined with experimental values for quartz-grossular. The resulting A-coefficients (%K²) are:

	Zrc	Alm	Grs	Ttn
Qtz	2.64	2.71	3.03	3.66
Zrc		0.07	0.39	1.02
Alm			0.32	0.95
Grs				0.63

for the relation $1000 \ln \alpha_{Y-X} = A_{Y-X} (10^6/T^2)$. The fractionation of oxygen isotopes between zircon and coexisting minerals can provide otherwise unavailable evidence of magmatic processes, including crystallization, remelting, and assimilation-fractional crystallization. Copyright © 2003 Elsevier Ltd

1. INTRODUCTION

Zircon is a common trace mineral in igneous, metamorphic, and clastic sedimentary rocks. Isotopic and trace element analysis of zircons can provide highly reliable and robust estimates of age, compositions of coexisting minerals and melts, and constraints on the genesis and protoliths of host rocks. Recent technological developments facilitate analysis of oxygen isotope ratios in zircon with high accuracy and precision by laser heating/gas-source mass-spectrometry (Valley et al., 1994) and in situ from microscope sections by ion microprobe/secondary ion mass-spectrometer (Eiler et al., 1997; Valley et al., 1998a; Peck et al., 2001).

Oxygen isotope studies of zircons have provided new insights for magmatic evolution (King et al., 1998; O'Connor and Morrison, 1999; King and Valley, 2001; Monani and Valley, 2001); the genesis of low $\delta^{18}\text{O}$ magmas (granites: Monani and Valley, 2001; Wei et al., 2002 felsic volcanic rocks: Bindeman and Valley, 2000, 2001, 2002, 2003); mantle geochemistry (Valley et al., 1998b; Upton et al., 1999); hydrothermal alteration and volcanogenic massive sulfide ore deposits (King et al., 1997, 2000); crustal growth and maturation in the Precambrian (Peck et al., 2000); the Snowball Earth hypothesis (Rumble et al., 2002); and surficial processes on the Early Archean Earth (Valley et al., 2002). The oxygen isotope geochemistry of zircon is reviewed by Valley (2003).

In spite of zircon's great utility, the fractionation of oxygen isotopes between it and other minerals is not well known. We report fractionations as A-coefficients, where:

$$\begin{aligned} \delta^{18}\text{O}_A - \delta^{18}\text{O}_B \\ = \Delta_{A-B} \approx 1000 \ln (\alpha_{A-B}) \\ = A_{A-B} 10^6/T^2 \quad (\text{T in K}) \quad (1) \end{aligned}$$

Eqn. 1 assumes linearity of $1000 \ln \alpha$ vs. $1/T^2$. This approximation is supported by experiments on mineral-mineral fractionation, though three coefficient curve fits are sometimes employed for tightly constrained experimental data (Clayton and Kieffer, 1991). Mineral abbreviations are defined in Table 1. The A-coefficients of this and other studies are most reliably used to calculate fractionations at temperatures near or higher than those of calibration because this relies on interpolation. Fractionation is 0‰ at infinite temperature and thus the calibrations in plots of Δ or $1000 \ln \alpha$ vs. $10^6/T^2$ are constrained to intersect the origin. Application of Eqn. 1 at lower temperatures than the calibration involves extrapolation and is inherently less certain.

Existing calibrations for oxygen isotope fractionation in zircon are highly variable. Valley et al. (1994) report an empirical calibration of zircon vs. almandine-rich garnet of $A_{\text{Zrc-Alm}} 0.0 \pm 0.2\%K^2$. King et al. (2001) empirically calibrated the A-coefficient for zircon vs. titanite, $A_{\text{Zrc-Ttn}} = 1.02 \pm 0.30$. The empirical value for $A_{\text{Zrc-Alm}}$ is in good agreement with theoretical calculations based on spectroscopic data by Kieffer (1982) for zircon and grossular ($A_{\text{Zrc-Grs}} = 0.0$) and from oxygen-cation bond calculations by Zheng (1993) ($A_{\text{Zrc-Alm}} = 0.00$). However, these calibrations are not in good agreement with estimates from the modified increment method (Hoffbauer et al., 1994; Richter and Hoernes, 1998) or with experiments (Sessions et al., 1996, 2003; Krylov et al., 2002). Furthermore, the experimental data are not self-consistent. The results of Sessions et al. (2003) suggest that zircon should have the

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Table 1. Values of $\delta^{18}\text{O}$ of zircons and almandine-rich garnets from granulite facies orthogneisses.

Sample	Zircon $\delta^{18}\text{O}$ (‰ VSMOW)	Garnet $\delta^{18}\text{O}$ (‰ VSMOW)	$\Delta(\text{Zrc-Alm})$ (‰)	Zircon ^a saturation T (°C)	Ref. ^b	Comments
AC85-7	8.36	8.27	0.09	na	1	A, AMCG, meta-anorthosite, meta zircons
AC85-10	8.29	8.23	0.06	804	1,3	A, AMCG, px-metasyenite, ig zircons
AC85-11	7.71	7.98	-0.27	na	1	A, AMCG, jotunitic gneiss, meta zircons
AC85-11	7.69	7.98	-0.29	651	1,3	A, AMCG, jotunitic gneiss, ig zircons
AM86-3	8.83	8.63	0.20	847	1,3	A, Stark complex, ig zircons
AM86-13	8.24	8.10	0.14	874	1,3	A, Hawkeye granite, ig zircons
AM86-17	7.78	7.72	0.06	833	1,3	A, AMCG, metagranite, ig zircons
AM87-9	8.29	7.90	0.39	847	1,3	A, AMCG, charnockitic gneiss, ig zircons
AM87-9	7.80	7.90	-0.10	na	1	A, AMCG, charnockitic gneiss, meta zrc
AM87-10	8.04	7.79	0.25	778	1,3	A, AMCG, charnockite, meta zircons
ANT	7.79	7.97	-0.18	780	1,3	A, Antwerp granitoid, ig zircons
CGAB	6.04	6.20	-0.16	na	1	A, AMCG, olivine metagabbro, meta zrc
TOE	8.29	7.90	0.39	na	1,2	A, Tomantown metagranite, meta zircons
96-MR43	8.38	7.94	0.44	860	2,3	Morin complex, Quebec, monzonite
Average			$0.07 \pm 0.07\%$ 1SE	808		

^a Zircon analyses are of the lowest magnetic fraction by Frantz separator. Zircon saturation temperatures calculated for igneous zircons only (Watson and Harrison, 1983). Abbreviations: A = Adirondack Mountains, N.Y.; AMCG = anorthosite-mangerite-charnockite-granite suite, ig = igneous; meta. = metamorphic. Minerals: Alm = almandine; And = andradite; Cc = calcite; Grs = grossular; Pyp = pyrope; Qtz = quartz; Sps = spessartine; Ttn = titanite; Zrc = zircon

^b References: (1) Valley et al. (1994); (2) this study; (3) Peck et al. (2003b).

lowest equilibrated $\delta^{18}\text{O}$ value of any rock-forming silicate, while the data of Krylov et al. (2002) suggest that it should be one of the highest.

We report analyses of $\delta^{18}\text{O}$ for zircons and coexisting minerals in three rock types to calibrate intermineral fractionations: granulite facies orthogneisses, granulite facies quartzites, and unmetamorphosed felsic volcanic rocks. Different thermal histories and processes of exchange have affected each suite, requiring different analytical strategies. These calibrations include a large data set of volcanic zircons with quenched mineral assemblages (and isotopic fractionations), and the first ion microprobe analyses of metamorphically equilibrated zircon grain boundaries. The agreement of empirical calibrations of zircon vs. garnet, titanite, and quartz from these varied lithologies strengthens the conclusion that careful empirical studies can derive equilibrium values for fractionation. Additional information about these samples is included in companion papers.

2. SAMPLES AND ANALYSIS

2.1. Zircons from Granulite Facies Orthogneiss

An empirical calibration of $\alpha_{\text{Zrc-Alm}}$ can be obtained from analysis of igneous zircons and metamorphic garnets in well-chosen orthogneisses (see Valley, 2001). Igneous zircons in plutonic rocks crystallize in equilibrium with other phases at magmatic temperatures, commonly 800–1000°C, and $\delta^{18}\text{O}(\text{Zrc})$ can be preserved with little change even during subsequent granulite facies deformation and recrystallization of the host rock (Valley et al., 1994; Peck et al., 2003a). Garnets in zircon-bearing orthogneisses grow in equilibrium with other minerals at metamorphic temperatures that are less than, and typically within 100°C of the estimated zircon saturation temperature (Watson and Harrison, 1983).

In Adirondack granulites, the equilibrium fractionation is

determined by analysis of zircon-garnet pairs even if the metamorphic garnet grew 100 Ma after the magmatic zircon (Valley et al., 1994). This is possible because zircon and garnet both equilibrated with the same whole rock (WR) composition, the igneous and metamorphic mineral assemblages are nearly the same, and these rocks were metamorphosed under fluid-absent conditions that preserved magmatic $\delta^{18}\text{O}(\text{WR})$ (Valley and O'Neil, 1984; Eiler and Valley, 1994) i.e., the rocks behaved as a closed system during granulite facies metamorphism. The garnet may have crystallized at slightly different temperatures, but the fractionation between zircon, garnet, and whole rock is small and varies by less than 0.2‰ between 800 and 900°C. Zircon saturation temperatures (Watson and Harrison, 1983) have been estimated for the nine rocks containing igneous zircons in Table 1 and average 808°C (Peck et al., 2003b). Thus magmatic temperatures are approximately equal to metamorphic temperatures (~725–775°C). The impact of this small difference in temperature between magmatism and metamorphism on $A_{\text{Zrc-Alm}}$ is further minimized because a few rocks are known to contain metamorphic zircons or metamorphic zircon overgrowths (Chiarenzelli and McLelland, 1993), which presumably crystallized in isotopic equilibrium with metamorphic garnets.

We report values of $\delta^{18}\text{O}$ for 14 zircon-garnet pairs (Table 1) from igneous rocks that have experienced granulite facies metamorphism. Samples were analyzed for oxygen isotope ratio in 2 mg aliquots using laser fluorination/gas-source mass spectrometry (Valley et al., 1995). A majority of these samples are from the AMCG suite (anorthosite-mangerite-charnockite-granite) in the Adirondacks (Valley et al., 1994). The AMCG magmatic event (~1155 Ma) preceded granulite facies metamorphism during the Ottawa Phase of the Grenville Orogeny by ca. 100 Ma (McLelland et al., 1996). Zircons from the Adirondacks have been classified as igneous, metamorphic, or disturbed based on size, shape, color, geochemistry, age, and

Table 2. Ion microprobe analysis of $\delta^{18}\text{O}$ for rims of detrital zircons in granulite facies quartzite and laser fluorination analyses of individual chips of coexisting quartz and garnet (Peck et al., 2003a).

Sample	Zircon $\delta^{18}\text{O}$ (‰ VSMOW)	1 std error, N	Garnet $\delta^{18}\text{O}$ (‰ VSMOW)	1 std error, N	Quartz $\delta^{18}\text{O}$ (‰ VSMOW)	1 std error, N	T (°C)	$\Delta(\text{Zrc-Alm})$ (‰)	$\Delta(\text{Qtz-Zrc})$ (‰)	$\Delta(\text{Qtz-Alm})$ (‰)
97ADK2	11.28	± 0.24 N = 48	11.24	± 0.06 N = 5	13.57	± 0.19 N = 4	725	0.04	2.29	2.33
97ADK4	10.30	± 0.20 N = 26	9.89	± 0.18 N = 4	12.03	± 0.08 N = 4	675	0.41	1.73	2.14

internal zoning as seen by cathodoluminescence (Chiarenzelli and McLelland, 1993). Valley et al. (1994) found that the $\delta^{18}\text{O}$ values of these different zircon groups are indistinguishable. The “disturbed” zircons (igneous zircons with age disturbed during metamorphism) are grouped with metamorphic zircons in Table 1. Two samples were found by Valley et al. (1994) to have anomalous zircon-garnet fractionations due to open system chemical modification of the rock between the time of zircon growth and garnet crystallization. One is a metagabbro that assimilated pelitic wall rocks after the crystallization of zircons, and the other is an ultramafic oxide-rich cumulate layer in anorthosite that was segregated by cumulate settling. These two samples were not closed systems between the time of igneous zircon crystallization and metamorphic garnet growth, and they are not included in Table 1.

2.2. Zircons from Granulite Facies Quartzite

Detrital zircons in quartzites may exchange oxygen isotopes over short distances during granulite facies metamorphism. Typically, slow diffusion of oxygen in zircon limits equilibration to a thin high $\delta^{18}\text{O}$ rim on each zircon. Similar thin re-equilibrated rims may form in zircons from orthogneisses, but are not significant (above) because the whole rock vs. zircon difference in $\delta^{18}\text{O}$ is much smaller in orthogneisses causing a smaller shift in $\delta^{18}\text{O}$. Ion microprobe analysis and an understanding of the history of the rock is required for accurate calibration of fractionations where zircons are zoned. In clastic sedimentary rocks, zircons can be abraded and rounded, but otherwise preserve the $\delta^{18}\text{O}$ value of the host rock in which they crystallized. A wide range of values is possible, but most commonly the source was originally a felsic to intermediate igneous rock with $\delta^{18}\text{O}(\text{Zrc}) = 6$ to 9‰. In metamorphosed sandstones, much of the quartz is also originally of igneous origin, but unlike zircons, quartz recrystallizes extensively during diagenesis or hydrothermal alteration with the result that $\delta^{18}\text{O}$ is elevated, sometimes by over 20‰ in quartz overgrowths (Graham et al., 1996). Upon high-grade metamorphism, recrystallization and diffusion homogenizes $\delta^{18}\text{O}$ in quartz resulting in $\delta^{18}\text{O}(\text{Qtz})$ values that are typically higher than 12‰ and unrelated to $\delta^{18}\text{O}(\text{Zrc})$. Diffusion of oxygen in non-metamict zircon is so slow that no exchange occurs until the highest grades of metamorphism. Even granulite facies quartzites contain zircons with igneous $\delta^{18}\text{O}$ values preserved in their core, with only thin rims that equilibrated during metamorphism (Peck et al., 2003a). Such robust preservation of $\delta^{18}\text{O}$ is consistent with anhydrous experiments for oxygen diffusion in zircon (Watson and Cherniak, 1997).

Zircons were analyzed from two 35 kg samples of granulite

facies quartzite from the southern Adirondack Mountains, 97ADK2 and 97ADK4 (Table 2; Peck et al., 2003a). 97ADK2 is coarse grained, nearly pure quartzite (~98% quartz) with minor amounts of metamorphic minerals including garnet and detrital minerals including rounded zircons. 97ADK4 is ~70% quartz with ~30% feldspar and traces of other minerals including metamorphic garnet and detrital zircon. An ion microprobe was used to analyze $\delta^{18}\text{O}$ from 20 μm diameter, 2–3 μm deep pits on the crystal faces (rims) and in the cores of large (>100 μm diameter) detrital zircons (see Valley et al., 1998a; Peck et al., 2001; 2003a). Quartz from the matrix was analyzed in 1–2 mg chips from several places in the hand sample using laser fluorination and gas-source mass spectrometry (see Valley et al., 1995; Spicuzza et al., 1998). Metamorphic garnets were also analyzed by laser fluorination.

2.3. Zircons from Volcanic Rocks

Phenocrysts of zircon and quartz commonly preserve magmatic values of $\delta^{18}\text{O}$ from the time of crystallization in quenched volcanic rocks, and are well suited for empirical calibrations of fractionation if magmatic values of $\delta^{18}\text{O}$ have not evolved during crystallization. Table 3 reports data for 28 samples from three felsic volcanic centers: Yellowstone (Bindeman and Valley, 2001), Timber Mountain/Oasis Valley Caldera complex (Bindeman and Valley, 2003), and the Bishop tuff (Bindeman and Valley, 2002).

Magmatic temperatures have been estimated four ways for the tuffs summarized in Table 3: liquidus temperatures at 3 wt% H_2O (MELTS, Ghiorso and Sack, 1995), magnetite-ilmenite cation thermometry (Anderson and Lindsley, 1988; Ghiorso and Sack, 1991), zircon saturation (Watson and Harrison, 1983), and $\Delta^{18}\text{O}(\text{Qtz-Magnetite})$ (Clayton et al., 1989; Chiba et al., 1989). The agreement is good among different temperature estimates, typically within 50°C for each sample. Table 3 plots the calculated liquidus temperatures for Yellowstone (Bindeman and Valley, 2001) and Timber Mountain (Bindeman and Valley, 2003), and magnetite-ilmenite temperatures for Bishop tuff, that agree well with earlier estimates (Bindeman and Valley, 2002).

Care was taken to avoid inherited xenocrysts of quartz or zircon, or quartz that experienced postmagmatic hydrothermal alteration. In plutonic, metamorphic, and some volcanic rocks, hydrothermal processes of alteration of $\delta^{18}\text{O}(\text{Qtz})$ operate on both a large and small scale to alter $\delta^{18}\text{O}(\text{Qtz})$ promoting heterogeneous and zoned crystals, but these features were not observed in analyzed samples by cathodoluminescence (CL). Rapidly cooled tuffs and lavas do not have enough time to exchange oxygen by diffusion, and recrystallization can be

Table 3. Values of $\delta^{18}\text{O}$ of zircon, quartz, and magnetite, and magmatic temperatures for volcanic rocks of the Long Valley, Timber Mountain/Oasis Valley, and Yellowstone caldera complexes.^a

Sample	Zircon $\delta^{18}\text{O}$ (‰ VSMOW)	± 1 std error, N	Quartz $\delta^{18}\text{O}$ (‰ VSMOW)	± 1 std error, N	Magnetite $\delta^{18}\text{O}$ (‰ VSMOW)	± 1 std error, N	$\Delta(\text{Qtz-Zrc})$ (‰)	T(°C) magmatic	Ref. ^b	Comment
BBF-1	2.58	± 0.04 N = 5	4.65	± 0.08 N = 5			2.07	856	1	Y, N. Biscuit Basin flow
BC-1	1.93	± 0.18 N = 5	3.70	± 0.11 N = 6			1.77	851	1	Y, Blue Creek flow
HQ-1	1.96	± 0.06 N = 3	4.13	± 0.06 N = 5			2.17	856	1	Y, Headquarters flow
HRT-C	5.66	± 0.06 N = 3	7.89	± 0.12 N = 5			2.23	827	1	Y, Huckleberry Ridge tuff C
IP96-1	3.87	± 0.04 N = 2	5.75	± 0.14 N = 4			1.88	869	1	Y, Bishop Mtn. flow
IP96-2	3.66	± 0.11 N = 3	5.34	± 0.19 N = 3			1.68	840	1	Y, Warm R. Butte flow
LCT-3a	4.14	± 0.01 N = 2	6.6	± 0.07 N = 4			2.46	825	1	Y, Lava Creek tuff A, upper
MFT-2	3.62	± 0.03 N = 3	5.98	± 0.07 N = 5			2.36	834	1	Y, Mesa Falls tuff
YL96-1	2.75	± 0.05 N = 3	5.14	± 0.07 N = 5			2.39	818	1	Y, W. Yellowstone flow
YL96-3	2.53	± 0.11 N = 2	4.86	± 0.03 N = 3			2.33	845	1	Y, Summit L. flow
YL96-7	3.90	± 0.07 N = 2	6.44	± 0.09 N = 6			2.54	843	1	Y, Mt. Haynes flow
YL96-8	3.92	± 0.13 N = 5	6.23	± 0.16 N = 4			2.31	838	1	Y, Harlequin flow
YL96-9	1.47	± 0.07 N = 5	4.42	± 0.05 N = 4			2.95	818	1	Y, Scaup L. flow
YL96-10	5.38	± 0.14 N = 2	7.24	± 0.16 N = 2			1.86	849	1	Y, Obsidian Cliff flow
YL96-11	4.13	± 0.05 N = 2	6.25	± 0.15 N = 4			2.12	843	1	Y, Lewis Canyon flow
YL96-12	2.88	± 0.10 N = 5	4.84	± 0.07 N = 4			1.96	843	1	Y, Aster Creek flow
YL96-13	2.59	± 0.08 N = 4	4.48	± 0.06 N = 4			1.89	846	1	Y, Mallard L. flow
YL96-15	5.03	± 0.06 N = 2	7.58	± 0.15 N = 6			2.55	840	1	Y, Paintpot Hill flow
YL96-16	2.06	± 0.03 N = 3	3.60	± 0.14 N = 5			1.54	846	1	Y, Solfatara Plateau flow
YL96-19	4.88	± 0.08 N = 2	7.60	± 0.08 N = 5			2.72	838	1	Y, Gibbon Hill dome
YL96-21	4.17	± 0.10 N = 3	6.53	± 0.20 N = 4			2.36	844	1	Y, Lewis Canyon flow
99TM-10	6.67	± 0.06 N = 5	8.93	± 0.06 N = 1	4.13	± 0.4 N = 2	2.26	978	2	TM, Topopah springs tuff, latite
99TM-13	6.57	± 0.03 N = 2	9.02	± 0.08 N = 2	2.98	± 0.05 N = 2	2.45	671	2	TM, Rainier Mesa tuff, rhyolite
99TM-16	6.49	± 0.04 N = 4	8.64	± 0.07 N = 3	2.5	± 0.00 N = 2	2.05	718	2	TM, Ranier Mesa tuff, rhyolite
99LV-748	5.94	± 0.01 N = 2	8.24	± 0.03 N = 7	2.94	± 0.08 N = 2	2.30	817	3	BT, Ig2NWa, late tuff
99LV-751	5.94	± 0.09 N = 3	8.25	± 0.04 N = 7	2.17	± 0.04 N = 2	2.31	743	3	BT, Ig2 Na, medium-late tuff
00LV-3	5.83	± 0.01 N = 2	8.16	± 0.04 N = 4	2.30	± 0.01 N = 2	2.33	763	3	BT, Ig2 NWb, very late tuff
00LV-27	5.59	± 0.08 N = 3	8.27	± 0.04 N = 3	1.81	± 0.04 N = 1	2.68	714	3	BT, Ig1E, early tuff

^a N = number of analyses of individual crystals or mineral separates; T calculated from MELTS program (see ref. 1) for Y; from magnetite-ilmenite cation compositions for TM; and $\Delta^{18}\text{O}(\text{Qtz-Mt})$ for BT.

Abbreviations: BT = Bishop tuff; TM = Timber Mountain/Oasis Valley caldera complex; Y = Yellowstone.

^b (1) Bindeman and Valley (2001); (2) Bindeman and Valley (2003); (3) Bindeman and Valley (2002).

recognized by CL or tests that recognize small-scale oxygen isotope heterogeneity (Valley and Graham, 1996; King et al., 1997; Bindeman and Valley, 2002). Likewise, analysis of single crystals can distinguish xenocrysts that tend to be more variable in $\delta^{18}\text{O}$ than phenocrysts (Bindeman and Valley, 2002).

Dramatic core to rim zoning of $\delta^{18}\text{O}(\text{Zrc})$ and disequilibrium between inherited xenocrysts of zircon and quartz (>0.2 – 2.4 Ma; Bindeman et al., 2001) is recognized in four low $\delta^{18}\text{O}$ post-Lava Creek lavas at Yellowstone (Bindeman and Valley, 2001) although rims of these zircons approach equilibrium in $\delta^{18}\text{O}$ with melt. These samples are not included in Table 3. Likewise, analyses are omitted from rocks of the low- $\delta^{18}\text{O}$ Ammonia Tanks cycle, where less dramatic, but significant ($\sim 2\%$) core to rim zoning in zircons is found. This zoning suggests inheritance of partially exchanged xenocrysts (by diffusion or overgrowth) that are late in the volcanic evolution at Timber Mountain caldera and show evidence of wall rock melting. In contrast, no mineral inheritance is recognized in the Bishop tuff, and $\delta^{18}\text{O}(\text{Zrc})$ values and zircon-mineral fractionations vary perfectly with temperature in this well studied zoned magma chamber (Bindeman and Valley, 2002).

Multiple analyses were made of each mineral to test for zonation or heterogeneity. For zircons, this included analyses of different splits separated based on size (sieved from < 53 μm diameter to >149 μm) or magnetism (Frantz separator). Many zircon splits were also air abraded and analyses of cores were compared to bulk. Quartz phenocrysts were analyzed both singly and as a concentrate that homogenized many crystals. Thus the values for standard error (Table 3) are a measure of how well each $\delta^{18}\text{O}$ value is known. For comparison, one standard deviation for five analyses of $\delta^{18}\text{O}$ in a homogeneous silicate mineral is typically 0.07% yielding one standard error of 0.03% in the University of Wisconsin lab (std. dev. $N^{1/2}$ = std. err.). Several samples have standard deviations greater than 0.15% and standard errors greater than 0.1% indicating real variability within the 10 to 15 kg sample that was crushed for zircon separation. While this variability causes a slightly greater range in the values of $\Delta_{\text{Qtz-Zrc}}$, it does not appear to bias the determined A coefficient.

The calibrations proposed here do not distinguish between α -quartz and β -quartz. The quartz phenocrysts in volcanic rocks clearly crystallized as β -quartz and since exchange at low temperatures below the α - β transition was not important, the data in Figure 1 apply to that mineral. The appropriate polymorph for data in Tables 1 and 2 is less clear. The temperatures and pressures of granulite facies metamorphism straddle the α - β transition (Cohen and Klement, 1967). If there is isotopic fractionation between these polymorphs, then a correction might be necessary. However, this has not been demonstrated. The reduced partition functions for α - and β -quartz can be calculated from phonon spectra, and the uncertainties are at least several permil (Kawabe, 1978; Krylov et al., 2002). Such large fractionation would be surprising for a low- ΔS_r , displacive transition like α - β quartz. Clayton et al. (1989) reviewed this topic, including experiments on α - and β -quartz vs. water (Matsuhisa et al., 1979), and concluded that “we find no evidence for an isotopic discontinuity corresponding to the α - β transition.”

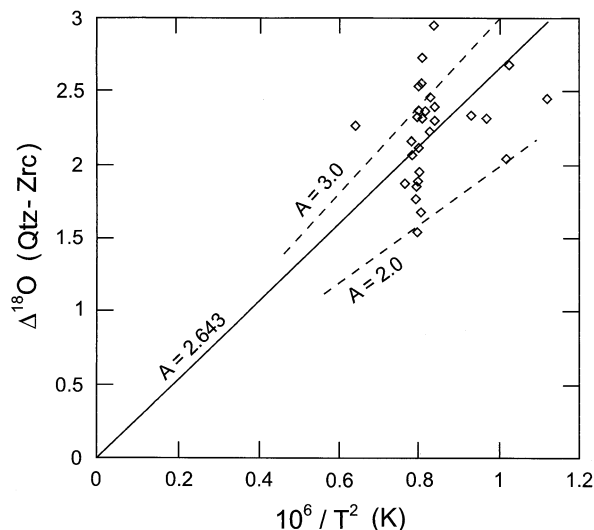


Fig. 1. Values of $1000 \ln \alpha_{\text{Qtz-Zrc}}$ vs. $10^6/T^2$ (see Table 3) for 28 felsic volcanic rocks from Yellowstone, Long Valley, and Timber Mountain caldera complexes (Bindeman and Valley, 2001, 2002, 2003). The best fit line is constrained to intersect the origin and yields $A = 2.64 \pm 0.08\%K^2$ (1 std. err). Dashed lines are for reference at arbitrary values of $A = 2.0$ and 3.0 .

3. RESULTS

The data for orthogneisses in Table 1 yield an average $\Delta_{\text{Zrc-Alm}} = 0.07 \pm 0.07\%$ (1 std. err.), in good agreement with $\Delta_{\text{Zrc-Alm}} = 0.0\%$ based on a subset of these data (Valley et al., 1994). As discussed above, this value equates to an A coefficient of $0.07\%K^2$ in Eqn. 1 if rocks have been a closed system to oxygen exchange from the time of magmatic zircon crystallization to that of metamorphic garnet growth at 725°C . If metamorphic temperature was actually 800°C , the A-coefficient would be decreased by only $0.01\%K^2$.

The ion microprobe analyses show that rims of detrital zircons in granulite facies quartzite (Table 2) are homogeneous, while the cores preserve a wide range of $\delta^{18}\text{O}$ values inherited from their varied, mostly igneous protoliths. For instance, in sample 97ADK2, the cores of zircons vary from 4.9 to 9.7% while the rims are homogeneous at $\delta^{18}\text{O} = 11.3 \pm 0.2\%$ (Peck et al., 2003a). The homogeneous rims are interpreted as detrital zircon that has exchanged oxygen by diffusion rather than new metamorphic zircon growth based on trace element compositions and cathodoluminescence imaging (Peck et al., 2003a). The average fractionation between the rims of zircons and the coexisting garnets is $0.22 \pm 0.18\%$ indicating that exchange has occurred. The agreement of measured $\Delta_{\text{Zrc-Alm}}$ between the granulite facies gneisses in Table 1 and the quartzites in Table 2 (0.07 vs. 0.22%) supports the conclusion that these values represent equilibrium at 725 – 800°C .

If the quartzites have not been altered, it follows that the measured values of $\Delta_{\text{Qtz-Zrc}}$ from Table 2 are also equilibrated. However, both diffusion and recrystallization of quartz can be significant in high-grade gneisses and the fractionations, $\Delta_{\text{Qtz-Zrc}}$, in the two samples of this study (97ADK2 vs. 97ADK4) are not consistent with each other ($\Delta_{\text{Qtz-Zrc}} = 2.29$ vs. 1.73%). Examination of the samples shows that 97ADK4 contains

modally significant feldspar, which will have exchanged oxygen with quartz after the thermal peak of metamorphism (see Valley, 2001). Furthermore, the feldspar is highly altered indicating post metamorphic infiltration of fluids. Thus $\delta^{18}\text{O}$ of both quartz and feldspar are not reliably preserved in 97ADK4. While it cannot be proven that peak metamorphic $\delta^{18}\text{O}(\text{Qtz})$ is preserved in the other sample (97ADK2), there is no additional mineral reservoir (i.e., feldspar) and the measured value of $\Delta_{\text{Qtz-Zrc}}$ yields an $A_{\text{Qtz-Zrc}}$ coefficient of $2.28 \pm 0.18\text{‰}$. Thus, one of the quartz-zircon pairs in quartzite yields a value consistent with metamorphic equilibration, but the potential for late exchange warrants caution in the interpretation of $\delta^{18}\text{O}$ values measured for quartz in granulite facies rocks.

Late exchange is not likely to have affected $\delta^{18}\text{O}$ in either the zircon or garnet, which, in contrast to quartz, have closure temperatures at or above the peak of metamorphism (Peck et al., 2003a). Thus the $A_{\text{Zrc-Gnt}}$ estimates are not affected. The larger data set, apparent homogeneity of minerals in the orthogneisses, and the use of high precision laser fluorination for analyses of zircon as well as garnet supports $A_{\text{Zrc-Alm}} = 0.07 \pm 0.07\text{‰K}^2$ from Table 1 as the best estimate. The data from quartzites provide independent, but less precise confirmation of this value.

Figure 1 shows values of $1000 \ln \alpha_{\text{Qtz-Zrc}}$ vs. $10^6/T^2$ for the 28 mineral pairs in volcanic rocks (Table 3). A linear fit to these data, forced through the origin, yields $A_{\text{Qtz-Zrc}} = 2.64 \pm 0.08\text{‰K}^2$ (1 SE). Dashed lines show arbitrary values of $A = 2.0$ and $A = 3.0$ for reference. The variability seen in Figure 1 is larger than the analytical uncertainty for laser fluorination analyses of zircon or quartz, which is better than $\pm 0.15\text{‰}$ (± 2 standard deviations at 95% confidence; Valley et al., 1995; Spicuzza et al., 1998). There are several possible causes of this variability, including sample heterogeneity and alteration. Post-magmatic hydrothermal alteration is unlikely to be significant as these samples coexist with fresh obsidian or frothy glass, which shows no signs of alteration. Actual variability among quartz phenocrysts and inheritance of zircon xenocrysts is documented for some samples at Yellowstone (Bindeman and Valley, 2000, 2001), and while we have not included those samples, it is possible that a small ($<0.5\text{‰}$) intrinsic variability exists among phenocrysts in other volcanic rocks. The good general agreement of all samples in Figure 1 shows that neither of these processes have been a large factor, but still, we have sorted the data in Table 3 in four tests to evaluate possible small effects. (1) Sample heterogeneity would be expected to cause poor precision for analyses of single quartz phenocrysts, chips, or different size splits of zircon. If all samples with 1 SE $> 0.1\text{‰}$ are culled from Table 3, the resulting value of A is only shifted up by 0.04‰K^2 . (2) Xenocrysts with anomalous $\delta^{18}\text{O}$ were discovered by Bindeman and Valley (2001, 2003) in certain low $\delta^{18}\text{O}$ rhyolites from Yellowstone and Timber Mountain. If all samples with $\delta^{18}\text{O}(\text{Zrc}) < 3\text{‰}$ or $\delta^{18}\text{O}(\text{Qtz}) < 5\text{‰}$ are removed from Table 3, the estimate of A shifts upwards by 0.04 or 0.01‰K^2 respectively. (3) Alternatively, it might be considered that the four samples of Bishop tuff are more homogeneous than those from the other centers, since zircons and quartz were extracted from individual, large pumice clasts with well determined temperature and depth of origin using melt inclusions in quartz (e.g., Anderson et al., 2000). Alteration of $\delta^{18}\text{O}$ has not been observed in surface quartz samples

Table 4. A-values (A_{Y-X} , ‰K^2 , Eqn. 1) for the fractionation of oxygen isotopes between zircon, quartz, almandine, grossular, and titanite.^a

Y:	X: Zrc	Alm	Grs	Ttn
Qtz	2.64	2.71	3.03	3.66
Zrc		0.07	0.39	1.02
Alm			0.32	0.95
Grs				0.63

^a References: $A_{\text{Qtz-Zrc}}$ and $A_{\text{Zrc-Alm}}$ (this study); $A_{\text{Qtz-Grs}}$ (Matthews, 1994); $A_{\text{Zrc-Ttn}}$ (King et al., 2001).

such as these from the Bishop tuff (McConnell et al., 1997). Regression of just the four samples of Bishop tuff result in an A-coefficient that is 0.09‰K^2 lower than the value for all data. (4) Likewise, regression of the 11 tuff samples from climactic eruptions (excluding more slowly cooled lavas) where no inheritance has been detected gives a value that is 0.09‰K^2 lower. Thus we regard the effects of alteration and inheritance as small and random in these samples, and that there is no justification for deleting any of the data in Table 3. The best estimate is: $A_{\text{Qtz-Zrc}} = 2.64\text{‰K}^2$ based on all 28 samples.

4. DISCUSSION

4.1. Experimental Studies

The calibrations in Table 4 do not support certain conclusions of recent experimental studies. Direct exchange experiments between calcite and zircon at $900\text{--}1100^\circ\text{C}$, 1 GPa yielded $A_{\text{Cc-Zrc}} = 4.14 \pm 0.25\text{‰K}^2$ (1 std err, $N = 7$) (Sessions et al., 2003). These values are revised from Sessions et al. (1996). When the seven values, which range from 2.92 to 4.98, are viewed individually, there is no temperature dependence and the higher temperature experiments suggest larger values of $A_{\text{Cc-Zrc}}$. Such temperature independence has not been observed in other mineral-calcite experiments which uniformly obey the theoretical prediction that fractionation will trend towards 0‰ at infinitely high temperature. The value of $A_{\text{Cc-Zrc}} = 4.14$ corresponds to $A_{\text{Qtz-Zrc}} = 4.52$ (Clayton et al., 1989), almost 2‰K^2 larger than $A_{\text{Qtz-Zrc}} = 2.64$ in Table 4. Such large fractionations are surprising as they would indicate that zircon fractionates lower $^{18}\text{O}/^{16}\text{O}$ ratios than any rock-forming silicate mineral, including olivine. No rock has been analyzed where zircon is found to be so low in $\delta^{18}\text{O}$ relative to its equilibrated host minerals. Even in case of mantle-derived zircon megacrysts; $\delta^{18}\text{O}(\text{Zrc})$ is higher than $\delta^{18}\text{O}(\text{olivine})$ of average mantle (Valley et al., 1998b see Valley, 2003).

Hydrothermal synthesis experiments of zircon at $700\text{--}1000^\circ\text{C}$ at 2 GPa yielded $\Delta_{\text{Zrc-H}_2\text{O}} = -3.70 + 2.74 (10^6/T^2)$ (Krylov et al., 2002). The fractionation for six individual values of $\Delta_{\text{Zrc-H}_2\text{O}}$ increases smoothly with temperature from -0.79‰ at 700°C to -1.98‰ at 1000°C . The results are linear vs. $10^6/T^2$ ($R^2 = 0.97$) with a Y-intercept of -3.7‰ . This temperature range exceeds that of Bottinga and Javoy (1973) whose results are only valid for $500\text{--}800^\circ\text{C}$. If calculated at higher temperatures, the new data yield very large fractionations (i.e., $\Delta_{\text{Zrc-H}_2\text{O}} = -2.8\text{‰}$ at 1500°C) and would indicate that zircon fractionation crosses that for other silicate

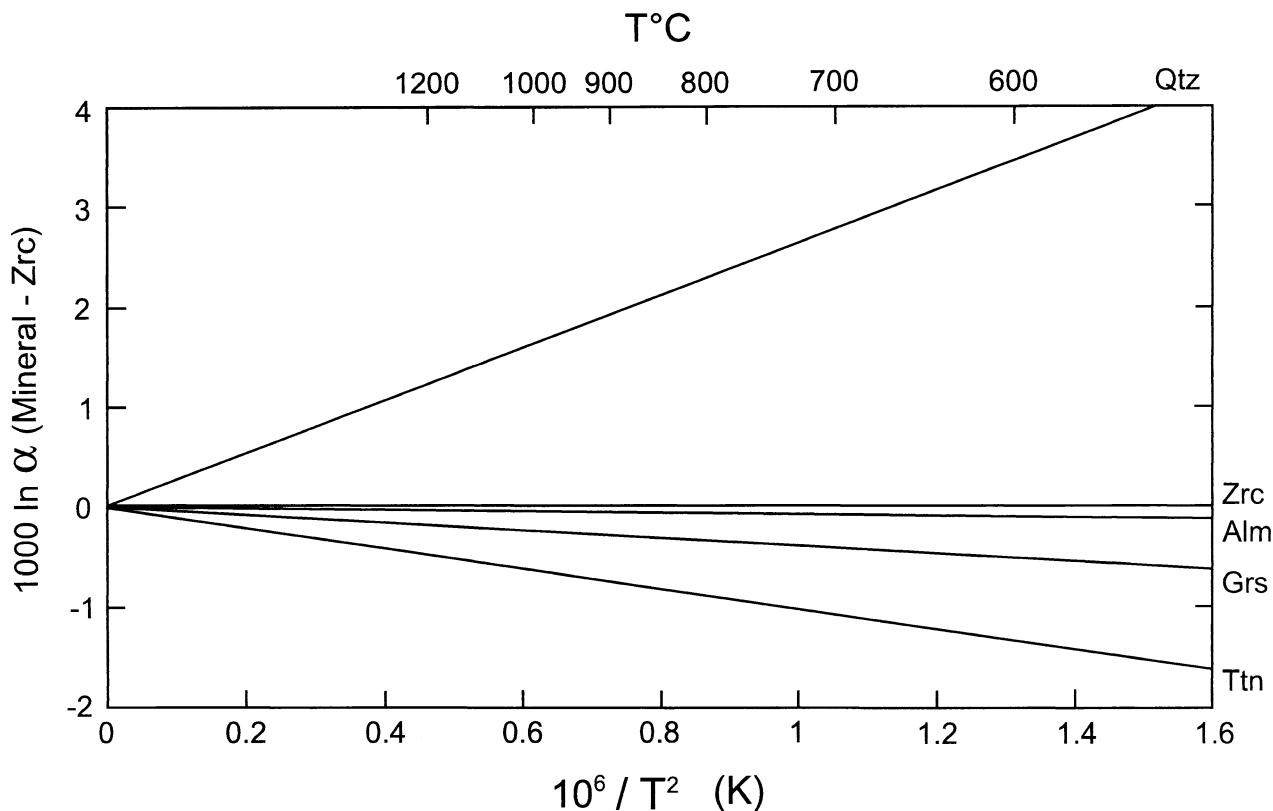


Fig. 2. Fractionation of oxygen isotopes in quartz, almandine, grossular, and titanite vs. zircon based on the empirical and experimental data of Table 4.

minerals. While cross-overs of fractionation are known at low temperature, these results are not consistent with the theoretical prediction that fractionation approaches 0‰ at high temperatures. Certain aspects of these experiments cannot be evaluated and could cause error. In particular, attainment of equilibrium is not demonstrated by unreversed synthesis experiments and dissolved silica from the quartz starting materials might cause “salt effects” and significant errors (Hu and Clayton, 2003). Krylov et al. (2002) calculate $A_{\text{Qtz-Zrc}} = 1.36\text{‰K}^2$ using $\Delta_{\text{Qtz-H}_2\text{O}}$ from Bottinga and Javoy (1973). At 1000K, this yields $\Delta_{\text{Qtz-Zrc}} = 1.36\text{‰}$, significantly lower than 2.64‰ of this study, however, larger values of $\Delta_{\text{Qtz-Zrc}} = 2.01$ and 2.38‰ at 1000K are derived with more recent calibrations of quartz–water (Clayton et al., 1972; Matsuhisa et al., 1979; Zheng, 1993; Hu and Clayton, 2003). In contrast to the results of Sessions et al. (2003), a value of $A_{\text{Qtz-Zrc}} = 1.36\text{‰K}^2$ would make zircon one of the more $^{18}\text{O}/^{16}\text{O}$ -rich minerals in a rock, equivalent to intermediate composition plagioclase. Again, there is no empirical evidence for such extreme fractionation in zircon. The empirically derived value of $A_{\text{Qtz-Zrc}} = 2.64\text{‰K}^2$ falls between the estimates of the two experimental studies, though agreement with the data of Krylov et al. (2002) is improved with recent calibrations of the quartz–water fractionation.

4.2. Empirical Studies

The results of three independent data sets (Tables 1–3) yield self-consistent estimates for the fractionation of oxygen isotope

ratios in zircon vs. almandine-rich garnet and quartz (Table 4, Fig. 2). The value of $A_{\text{Zrc-Alm}} = 0.07 \pm 0.07\text{‰K}^2$ is measured by laser fluorination on mineral separates from orthogneisses. The $A_{\text{Zrc-Alm}}$ coefficient from ion microprobe analysis of zircons in quartzite agrees well ($0.22 \pm 0.18\text{‰K}^2$), providing independent confirmation of this value. The value of $A_{\text{Qtz-Zrc}} = 2.64 \pm 0.08\text{‰K}^2$ is based solely on high accuracy and precision laser fluorination analyses of $\delta^{18}\text{O}$ from fresh volcanic rocks that cooled quickly. The less precise ion microprobe value for quartzite sample 97ADK2 ($2.28 \pm 0.24\text{‰K}^2$) is consistent with this value, again providing independent confirmation.

When $A_{\text{Qtz-Zrc}}$ and $A_{\text{Zrc-Alm}}$ are combined with experimentally determined $A_{\text{Qtz-Grs}}$ and empirically determined $A_{\text{Zrc-Ttn}}$, the remaining values in Table 4 can be calculated. Two sets of experiments have yielded values of $A_{\text{Qtz-Grs}}$ (Matthews, 1994; Rosenbaum and Matthey, 1995). The $A_{\text{Qtz-Grs}} = 3.03$ coefficient of Matthews is in perfect agreement with $A_{\text{Qtz-Grs}} = 2.99$ obtained by adjusting the value of Rosenbaum and Matthey downwards by 0.16 to compensate for the composition of their garnet ($\text{Grs}_{78}\text{And}_{19}\text{Pyp}_3$, Kohn and Valley, 1998). The value of $A_{\text{Qtz-Grs}} = 3.03$ is also in good agreement with $A_{\text{Qtz-Sps}} = 2.83$ for Mn-rich garnets (Lichtenstein and Hoernes, 1992). The value of $A_{\text{Zrc-Ttn}} = 1.02 \pm 0.06\text{‰K}^2$ was calculated from measurements of 27 coexisting pairs of zircon and igneous titanite and assuming a closure temperature of 650 °C for oxygen diffusion in titanite (King et al., 2001).

The data in Table 4 result in $A_{\text{Alm-Gr}} = 0.32\text{‰K}^2$, which agrees well with the value of ~ 0.5 estimated by Kohn and Valley (1998a) that was based on 4 samples. Likewise the value of $A_{\text{Qtz-Ttn}} = 3.66\text{‰K}^2$ in Table 4 agrees with 3.57 estimated by King et al. (2001). The two fractionations that we have empirically calibrated, $A_{\text{Qtz-Zrc}}$ and $A_{\text{Zrc-Alm}}$, are in excellent agreement with each other when compared via published experimental and empirical calibrations (Qtz-Gr and Alm-Gr).

Thus, the empirical data from three different rock types and geologic environments provides independent and self-consistent estimates of oxygen isotope fractionation in zircon that is intermediate among rock-forming silicates. It would be an unlikely coincidence if self-consistent fractionations were derived from such different rocks if these minerals preserve growth zoning or have undergone variable retrograde exchange. The good agreement among results from samples with different history is strong support for our conclusion that the A-coefficients in Table 4 represent equilibrium fractionation.

5. APPLICATIONS TO PROGRESSIVE CONTAMINATION OF GRANITIC MAGMAS

Oxygen isotope analysis is a well-established technique to determine the amount of crustal material in granitic batholiths (Taylor and Sheppard, 1986), but conventional analysis can not determine the timing or trace the evolution of this process. Such information is important for distinguishing among different sources, contaminants, and mechanisms.

The oxygen isotope analysis of refractory magmatic minerals can provide a new monitor of crustal contamination at different stages in an evolving magma. The high $\delta^{18}\text{O}$ of metasedimentary wall rocks contrast with the composition of primitive magmas and even small amounts of melting and assimilation will measurably raise the $\delta^{18}\text{O}$ of the magma. This process has been documented in numerous studies that correlate higher $\delta^{18}\text{O}$ of a whole rock to mineralogical or chemical properties sometimes characterized as “S-type” (see Taylor and Sheppard, 1986). However, the interpretation of whole rock isotope compositions is hampered because of potential problems due to contamination and postmagmatic alteration, and because the whole rock chemistry represents the integrated history of the rock. Analysis of individual refractory minerals minimizes problems of alteration. Furthermore, when independent evidence indicates the order of crystallization, the compositions of these minerals will track the evolving composition of the magma.

Granites containing igneous garnet and zircon are ideal for quantitative evaluation of magmatic evolution. Four samples from Cretaceous granitic rocks of the Idaho batholith were analyzed by King and Valley (2001) who found that $\delta^{18}\text{O}(\text{Gnt}) > \delta^{18}\text{O}(\text{Zrc})$ and that $\Delta_{\text{Gnt-Zrc}}$ correlates to $\delta^{18}\text{O}(\text{Zrc})$. These trends are subtle and their interpretation depends on accurate knowledge of fractionation between garnet and zircon reported here ($A_{\text{Zrc-Alm}} = 0.07$). Figure 3 shows the Idaho data along with the equilibrium fractionation at 1000 and 500°C. It is apparent that samples are not equilibrated at the 2 standard deviation uncertainties shown and that the higher $\delta^{18}\text{O}$ samples are further from equilibrium. This trend is discussed by King and Valley who conclude the best interpretation is that these magmas incorporated varying amounts of high $\delta^{18}\text{O}$ Belt series

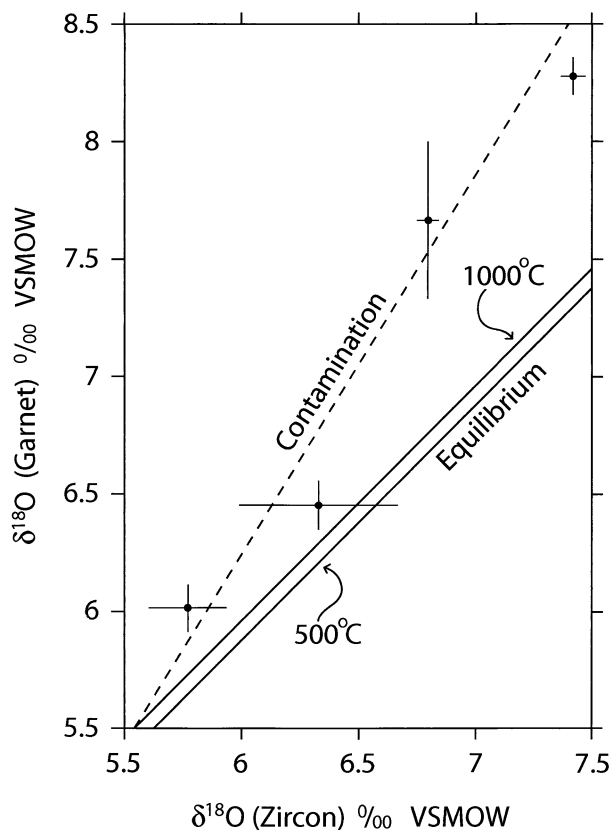


Fig. 3. Plot of $\delta^{18}\text{O}(\text{garnet})$ vs. $\delta^{18}\text{O}(\text{zircon})$ for magmatic-garnet bearing granitoids of the Idaho batholith (King and Valley, 2001). Isotherms for 500 and 1000°C are from this study. Garnet values are up to 1‰ higher than coexisting zircon. These minerals are not equilibrated at any temperature and the correlation of $\Delta^{18}\text{O}_{\text{Gnt-Zrc}}$ to $\delta^{18}\text{O}(\text{Zrc})$ suggests that garnets, which crystallized after zircon, record magma compositions that were elevated by contamination with high $\delta^{18}\text{O}$ Belt series metasediments (see text).

metasedimentary rocks. Textures in thin section show that zircon crystallized before garnet and thus the zircon records the composition of the magma at a lower level of contamination. If the average $\delta^{18}\text{O}$ of the metasediment was 17‰ (average Belt series) then the two samples with $\delta^{18}\text{O} < 6.5$ and $\Delta_{\text{Gnt-Zrc}} \sim 0.2\text{‰}$ experienced $\sim 2\%$ contamination after the time of zircon crystallization and before garnet crystallized. If all samples originated from the same source rocks, then the higher $\delta^{18}\text{O}$ samples with $\Delta_{\text{Gnt-Zrc}} \sim 1\text{‰}$ record a two-stage history. They experienced up to 20% contamination in total and the last 5–10% occurred between the time of zircon and garnet crystallization. Thus analysis of multiple refractory minerals provides evidence of different periods in the evolving magmatic history.

Studies of garnet-bearing granitoids are underway in the Sierra Nevada batholith (Lackey et al., 2002). Ten peraluminous samples from the Cretaceous Dinkey Dome quartz monzonite show evidence that magmas were derived from high $\delta^{18}\text{O}$ rocks in the deep crust before the growth of zircons and that magmas were subsequently (between the time of zircon and garnet growth) contaminated by lower $\delta^{18}\text{O}$ wall rocks, possibly altered volcanic rocks (Hinke et al., 2002). Future

studies will analyze zircon, garnet, and titanite in situ by ion microprobe to detect growth zoning, which would reveal magmatic evolution in more detail, and could correlate with trace elements and age.

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