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4.4 billion years of crustal maturation: oxygen isotope ratios of magmatic zircon

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Abstract Analysis of $\delta^{18}O$ in igneous zircons of known age traces the evolution of intracrustal recycling and crust-mantle interaction through time. This record is especially sensitive because oxygen isotope ratios of igneous rocks are strongly affected by incorporation of supracrustal materials into melts, which commonly have $\delta^{18}O$ values higher than in primitive mantle magmas. This study summarizes data for $\delta^{18}O$ in zircons that have been analyzed from 1,200 dated rocks ranging over 96% of the age of Earth. Uniformly primitive to mildly evolved magmatic $\delta^{18}O$ values are found from the first half of Earth history, but much more varied values are seen for younger magmas. The similarity of values throughout the Archean, and comparison to the composition of the "modern" mantle indicate that $\delta^{18}O$ of primitive mantle melts have remained constant ($\pm 0.2‰$) for the past 4.4 billion years. The range and variability of $\delta^{18}O$ in all Archean zircon samples is subdued ($\delta^{18}O(Zrc) = 5–7.5‰$) ranging from values in high temperature equilibrium with the mantle ($5.3 \pm 0.3‰$) to slightly higher, more evolved compositions (6.5–7.5‰) including samples from: the Jack Hills (4.4–3.3 Ga), the Beartooth Mountains (4.0–2.9 Ga), Barberton (3.5–2.7 Ga), the Superior and Slave Provinces (3.0 to 2.7 Ga), and the Lewisian (2.7 Ga). No zircons from the Archean have been analyzed with magmatic $\delta^{18}O$ above 7.5‰. The mildly evolved, higher Archean values (6.5–7.5‰) are interpreted to result from exchange of protoliths with surface waters at low temperature followed by melting or contamination to create mildly elevated magmas that host the zircons. During the Proterozoic, the range of $\delta^{18}O(Zrc)$ and the highest values gradually increased in a secular change that documents maturation of the crust. After ~1.5 Ga, high $\delta^{18}O$ zircons (8 to $>10‰$) became common in many Proterozoic and Phanerozoic terranes reflecting $\delta^{18}O$(whole rock) values from 9 to over 12‰. The appearance of high $\delta^{18}O$ magmas on Earth reflects non-uniformitarian changes in the composition of sediments, and rate and style of recycling of surface-derived material into magmas within the crust.

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Introduction

Oxygen isotopes in zircon

Zircon is a common accessory mineral in igneous rocks and preserves the most reliable record of both magmatic oxygen isotope ratio (δ^{18}O, Valley 2003) and magmatic age (U-Th-Pb, Hanchar and Hoskin 2003). Several factors combine in zircon to create a robust and retentive geochemical record, including: high temperatures of mineral stability and melting, slow diffusion rates for cations and anions, chemical inertness, and hardness. High contrast cathodoluminescence and other imaging techniques distinguish domains of growth zoning from igneous and subsolidus overgrowth, resorption, and radiation damage. While many common minerals are readily altered by metamorphic, hydrothermal, or diagenetic processes, zircons are generally not affected. Zircons with heavy radiation damage or postmagmatic alteration can be identified and avoided prior to analysis. No other mineral permits δ^{18}O(magma) to be coupled to age of crystallization with such confidence.

Oxygen isotope ratios of magmas reflect the δ^{18}O of magmatic source rocks and contaminants. With rare exceptions, the mantle is a remarkably homogeneous oxygen isotope reservoir (Eiler 2001) and igneous zircons in high temperature equilibrium with mantle magmas have average $\delta^{18}O = 5.3 \pm 0.3‰$ (1 SD, Valley et al. 1998). Even small deviations from the mantle value of δ^{18}O are readily apparent. Fractional crystallization can result in higher whole rock (WR) values of δ^{18}O by up to ~1‰ in more silicic magmas, however the value of δ^{18}O(Zrc) remains approximately constant because the fractionation, Δ^{18}O(WR-Zrc), increases at nearly the same rate as δ^{18}O(WR) due to the greater abundance of higher δ^{18}O minerals, e.g., quartz and feldspar, in the evolving, more silicic magmas. The change in δ^{18}O(WR) is increased if temperature decreases significantly during differentiation, however the effects of variable temperature on δ^{18}O(Zrc) are minor due to small intermineral fractionations at magmatic temperatures and because zircon fractionations are intermediate among rock-forming minerals (i.e., zircon is neither the highest nor lowest δ^{18}O mineral in a rock, Valley 2003; Valley et al. 2003). Therefore, significant deviations of δ^{18}O(Zrc) from the mantle value are the direct or indirect result of intra-crustal recycling, i.e., magma interaction with supracrustal materials that ultimately derived their evolved δ^{18}O from low temperature processes on or near the surface of the Earth where oxygen isotope fractionations are large.

Oxygen isotope reservoirs

The δ^{18}O values of common crustal materials are summarized in Fig. 1. Both δ^{18}O(WR) and δ^{18}O(Zrc) are shown. The fractionation, Δ^{18}O(Zrc-WR), varies with mineralogy and can be approximated as a linear function of wt % SiO_2 for igneous rocks at magmatic temperatures. Values of Δ^{18}O(Zrc-WR) vary from ~−0.5‰ for mafic rocks to ~−2‰ for granites according to the relation:

$$\Delta^{18}O(Zrc - WR) = \delta^{18}O(Zrc) - \delta^{18}O(WR) \approx -0.0612(wt.\%SiO_2) + 2.5$$

(Valley et al. 1994; Lackey 2005). For comparison with the crust, two vertical lines show the mantle range of δ^{18}O(Zrc) at $5.3 \pm 0.3‰$. Fresh basalts (WR) are close, but slightly above the range for mantle zircon, but altered basalts plot at higher or lower values depending on the temperatures of interaction with surface waters. Likewise, in ophiolite sequences, low δ^{18}O gabbros have been altered by high temperature hydrothermal fluids while the high δ^{18}O basalts were altered at low temperatures (Gregory and Taylor 1981; Eiler 2001). The generalization that low temperature water–rock interactions cause high δ^{18}O also applies for continental and oceanic sediments that uniformly plot at much higher values reflecting interaction with surface water. The range of igneous zircons for various rock types is more subdued in δ^{18}O, reflecting the magmatic values, and generally above the mantle value. Low δ^{18}O magmas have been intensely studied in a few localities, especially sub-volcanic environments, but are not a volumetrically significant component of the crust (Balsley and Gregory 1998).

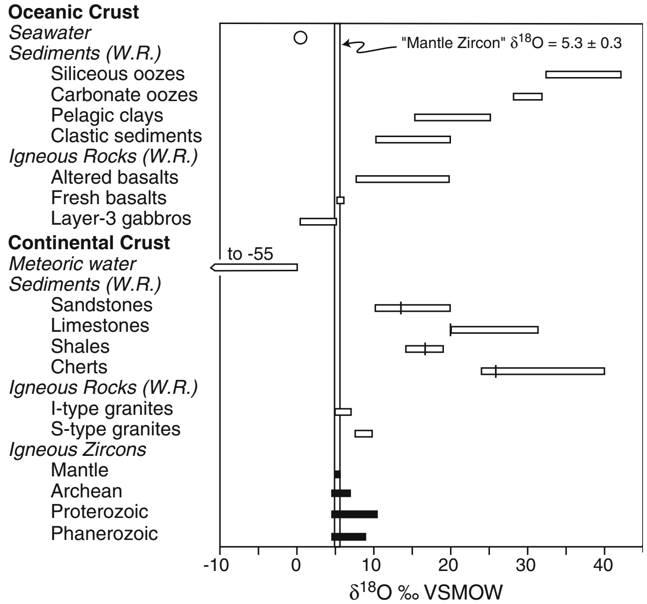

Fig. 1 Typical values of δ^{18}O for sediments, igneous rocks, and igneous zircons (modified from Eiler 2001). Ticks for continental sediments represent average values for the Archean. The narrow field at $5.3 \pm 0.3‰$ represents δ^{18}O of zircons in high-temperature equilibrium with the mantle (plotted at 1SD). Zircons from primitive magmas fall near this field, and values above 6.5‰ result from recycling of supracrustal material. The distribution of low δ^{18}O zircons is uncertain before 150 Ma and are not shown (see text)

Average values are shown for modern sandstones, limestones, and shales in Fig. 1. The compositions of Precambrian sedimentary rocks are lower than modern sediments and have average δ^{18}O(WR) values of: 16.7‰ for shales (Land and Lynch 1996); 20‰ for carbonates (Shields and Veizer 2002), 13–14‰ for sandstones (Blatt 1987); and 24–28‰ for cherts (Blatt 1987; Perry and Lefticariu 2003). Some chemical sediments are systematically lower in δ^{18}O as a function of increasing age leading to provocative proposals of secular changes in δ^{18}O of sediments and oceans through time (Walker and Lohmann 1989; Burdett et al. 1990; Land and Lynch 1996; Muehlenbachs 1998; Wallmann 2001; Shields and Veizer 2002; Perry and Lefticariu 2003; Knauth and Lowe 2003; Veizer and Mackenzie 2003). Changes through time in the composition or availability of sediments for magmatic recycling will influence the δ^{18}O of any resultant igneous rocks.

Evolved δ^{18}O in magmas

High values of magmatic δ^{18}O, above that derived from the mantle, are most often found in granitic rocks and attributed to melting or assimilation of sediments, altered volcanics, or other supracrustal rocks of near-surface genesis. We distinguish such ''intra-crustal recycling'', where supracrustal materials are melted or contaminate magma that intrudes continental crust, from ''mantle recycling'', where continental crust is subducted and returned to the mantle.

Many questions of granite genesis and the definition of granite types are beyond the scope of this contribution. The δ^{18}O values of S- and I-type granites in Fig. 1 are characteristic of type localities in SE Australia and other Phanerozoic examples (O'Neil and Chappell 1977; O'Neil et al. 1977). As early as 3.1 Ga, granite plutons are estimated to represent ~20% of Archean exposure (Condie 1993) including many that are peraluminous (Sylvester 1994) and might contain a sedimentary component. However, we avoid widespread application of the S and I classifications (see Chappell and White 2001).

Magmatic values of δ^{18}O can also be shifted by assimilation or remelting of altered igneous rocks. Magmatic cannibalization is common in plutonic complexes where successive magmas intrude and may melt each other. In this situation, early crystallized magmas are often hydrothermally altered by water circulation powered by the heat of later magmas. The δ^{18}O (and δD) of altered wall rock is shifted while other geochemical systems are generally unaffected. Radiogenic isotope systems cannot detect this process because of insufficient time for ingrowth of daughter isotopes. Thus, some melts that are partially or wholly produced in the crust (from mantle-derived materials) may appear mantle-derived. Analysis of δ^{18}O in zircons allows clear distinction of magmatic versus postmagmatic composition and, in many instances, provides the only evidence for cannibalization or wall rock contamination (Valley 2003). The distinction of first and second-generation magmas is significant beyond the sphere of isotope geochemistry, affecting estimates of the rate of heat and mass transfer, and crustal growth.

This study reports oxygen isotope ratios for igneous zircons with ages from 4.4 Ga to nearly the present. We demonstrate the utility of zircon oxygen isotope ratios as a monitor of magmatic chemistry, and highlight contrasting behavior between oxygen, the major element in the crust and the mantle, and commonly applied trace element and radiogenic isotope systems. One goal is to test the generality of the observation that Archean magmas in North America had uniform values of δ^{18}O within 2‰ of the mantle (5.3‰) while post-Archean magmas were higher and more variable (Peck et al. 2000). A second goal is to examine the timing and causes of this secular trend.

Techniques

Magmatic zircons of known age have been analyzed for δ^{18}O from 1,200 rocks (Table 1, Appendix 1). For most samples, U-Pb age was measured in previous studies by thermal ionization mass-spectrometry (TIMS) or by ion microprobe (SIMS). For a few samples, age was inferred based on geochronology of associated rocks. All detrital zircons (4.4–2.9 Ga) from the Jack Hills and the Beartooth Mountains were analyzed in situ by ion microprobe for age and δ^{18}O. Whole rock chemical data are available for some samples.

A majority of the δ^{18}O analyses were made at the University of Wisconsin–Madison. Zircons separated from igneous rocks were analyzed for δ^{18}O in samples consisting of 1–2 mg, typically 100–1,000 zircons, that were concentrated by standard crushing, gravimetric, and magnetic procedures. For samples previously dated by TIMS, aliquots of the original zircon separate were obtained. Concordance of U-Pb ages provides an index of radiation damage, and analysis of concordant samples enhances confidence in the reliability of δ^{18}O values as primary (Valley 2003; Cavosie et al. 2005). In many samples, more than one magnetic or size split was analyzed to test for variability and guard against significant deviation of δ^{18}O due to inheritance of older cores. The least magnetic zircons available were analyzed so as to correspond as closely as possible to those that were dated. In rare cases where detectable differences in δ^{18}O are seen among different zircons from the same sample, δ^{18}O for the least magnetic zircons is reported because they display little or no evidence of radiation damage (Valley et al. 1995). For zircon samples that were originally separated for oxygen isotope or fission track studies, age is typically reported from geochronology on the same unit. Since 1999, zircons in the Wisconsin lab have been soaked in concentrated HF at room temperature for 8–12 h to dissolve impurities and metamict material. Cold HF does not affect δ^{18}O of undamaged zircons (King et al. 1998; Valley 2003). Clouded grains

Table 1 Age and oxygen isotope ratio of igneous zircons tabulated in Appendix 1, given as ESM, available at http://dx.doi.org/10.1007/s00410-005-0025-8

Location	Age Range Ma	$\delta^{18}O$ Zircon Ave.	1Std. Dev. permil	# Rocks	Dominant Lithologies	# Outliers $\delta^{18}O$*
ARCHEAN						
Jack Hills, Yilgarn craton, Australia	4404–3280	6.2	0.7	59	Detrital zircons	
Beartooth Mountains, Wyoming province	3973–2936	6.2	0.5	10	Detrital zircons	
Barberton, South Africa	3538–2740	5.53	0.67	11	Granite, tonalite	
Superior Province Volcanics	2736–2691	5.57	0.48	45	Rhyolite, dacite	3
Superior Province Plutonic						
Wabigoon Subprovince	3003–2680	5.65	0.52	36	TTG**, sanukitoid, gabbro	
Quetico Subprovince	2688	6.83		1	Quartz-monzonite	
English River Subprovince	2698–2697	6.69	0.21	3	TTG, sanukitoid, gabbro	
Uchi Subprovince	2741–2700	5.90	0.34	5	TTG, sanukitoid	
Wawa Subprovince	2728–2678	5.94	0.48	6	TTG, sanukitoid	
Abitibi Subprovince	2720–2668	6.03	0.98	8	Syenite, monzonite, quartz-diorite	
Lewisian	2700	5.48	0.46	2	Tonalitic orthogneiss	
Slave Province	2694–2670	4.87	0.26	5	Tonalite	
PROTEROZOIC						
China	2560–2494	5.64	0.21	3	Granite, granodiorite	
Brazil	2251–1894	5.33	0.71	16	Granitic-mafic orthogneiss	
Trans Hudson	2597–1819	6.15	0.72	11	Granitic-tonalitic gneiss	
Ukranian Shield	2695–1720	6.64	1.03	12	Granite, granodiorite, gabbro	
Australia	1858–1806	7.11	0.79	6	Granite, granodiorite	
Wisconsin	1860–1760	5.08	0.11	2	Granite, tonalite	
Finland	1886–1573	6.94	0.95	23	Granite	
Great Basin, western U.S.	1500	6.60	1.11	19	Pegmatite, orthogneiss	
Laramie Anorthosite Complex	1340	7.35	0.21	5	Monzosyenite	
Nain Anorthosite Complex	1330–1285	6.24	0.67	20	Granite, ferrodiorite, anorthosite	
Grenville Province						
Adirondack Mountains	1336–900	7.86	1.20	60	Granitic to mafic orthogneiss	1
Frontenac	1176–1160	11.34	1.63	8	Granitic to monzonitic orthogneisses	
Quebec	1240–1077	7.64	1.41	13	Granitic orthogneiss, anorthosite	
Grenville-age, Vermont	1154–1119	7.76	0.49	3	Augen gneiss	
Grenville-age, Virginia and Maryland	1162–998	7.39	0.65	24	Augen gneiss, granitic orthogneiss	
Virginia and Maryland (Neoproterozoic)	748–680	6.39	0.51	3	Granite	
Uruguay (Various Ages)	2111–510	7.84	0.98	6	Granitic orthogneiss	
Argentina (Various Ages)	1000–206	7.96	1.76	9	Granodiorite, orthogneiss	
Brazil (Neoproterozoic)						
Curitiba Microplate	590	6.20	0.28	2	Granite, diorite	
NE Paran State	633–564	7.40	1.14	13	Granite to granodiorite	
Paranagu and Monguagu Batholiths	620–567	7.20	0.98	10	Granite, tonalite	
Serra do Mar Alkaline-Peralkaline Suite	604–540	5.58	0.79	21	Granite, rhyolite	
Pien Batholith	618–605	6.02	0.55	7	Granite to diorite	
Brusque Metamorphic Complex	638–580	7.25	0.35	2	Granite, syenite	
Florianpolis Batholith	640–609	7.39	0.62	6	Granite	
Pelotas Batholith	620–580	7.64	0.52	7	Granite	
SE border of San Francisco Craton	653–632	7.03	1.05	2	Orthogneiss	
Sao Rafael Pluton	627	5.98	0.17	9	Granite, quartz-monzonite	
Emas Pluton	633	10.04	0.22	8	Granodiorite	
Borborema province	880–581	8.73	0.92	34	Shoshonite,high-K calc-alkaline	
Nubian shield, Israel	620	7.59	0.80	3		
PHANEROZOIC						
Grelo, Spain	310	6.17		1	Granodiorite	
Greece	316–233	6.51	1.16	3	Granitic orthogneiss	
Antarctica	183	6.09		1	Felsic dike	
Western U. S.						
Northern Sierra Nevada batholith	143–140	5.55	0.69	3	Granodiorite	
Western Sierra Nevada batholith	145–93	6.77	0.82	36	Tonalite to gabbro	
Eastern Sierra Nevada batholith	222–81	6.19	0.48	85	Granite to granodiorite	
Central Sierra Nevada batholith	162–89	6.94	0.60	91	Granite to diorite	
Southern Sierra Nevada batholith	117–81	7.82	0.72	45	Granite to diorite	
Peraluminous Plutons, Sierra Nevada	165–86	7.95	0.46	35	Granite	
Owens Valley/White Mountains	217–74	6.83	0.69	31	Granite to granodiorite	
Death Valley	173	7.07		1	Monzonite	
Idaho Batholith	100–45	6.97	0.78	29	Granite to granodiorite	

Table 1 (Contd.)

Location	Age Range Ma	$\delta^{18}O$ Zircon Ave.	1Std. Dev. permil	# Rocks	Dominant Lithologies	# Outliers $\delta^{18}O$*
Great Basin	480–27	6.84	1.23	124	Granite	
Timber Mountain/ Oasis Valley	12.8–11.3	5.75	1.07	9	Rhyolite, latite	
Bishop Tuff	0.76	5.83	0.17	4	Rhyolite	
Yellowstone	2–0.109	3.17	1.48	26	Rhyolite	
China						
Eastern China	126–98	4.62	0.57	37	A-type granite	
Dabie Orogenic Belt	120	5.15	0.46	37	Post metamorphic granite	
British Tertiary Igneous Province						
Arran	58	6.48	0.97	3	Granite	
Isle of Skye	58	3.23	1.48	21	Granite	
Isle of Mull	58	4.25	1.44	3	Granite	

*Not included in average.
***TTG* tonalite, trondhjemite, granodiorite

were removed by hand picking and resistant zircons were ground for analysis. Most zircon separates were analyzed at least twice. Zircon powder is heated by CO_2 laser in a BrF_5 atmosphere to yield O_2 that is cryogenically purified, reacted with hot graphite, and analyzed as CO_2 in a dual-inlet gas-source mass-spectrometer. Analyses are standardized by replicate analyses (3 or more) on the same day of UWG-2 garnet standard ($\delta^{18}O = 5.8‰$) and reported in standard per mil notation relative to VSMOW (Valley et al. 1995). Typical precision for these analyses is $\pm 0.05‰$ (1SD) and accuracy relative to NBS-28 quartz standard is $\pm 0.1‰$.

All of the published and unpublished data for $\delta^{18}O$(Zrc) that we are aware of are included in Appendix 1, except as noted in text. Approximately 60% of the $\delta^{18}O$(Zrc) data are previously published and another 20% are in manuscripts that are in preparation or review (Appendix 1). The selection of samples was guided by the goals of these previous studies and by the availability of zircon concentrates. Thus the coverage is not perfectly distributed through time and across all major geologic terranes.

For detrital igneous zircon crystals (e.g., Jack Hills metaconglomerate and Beartooth Mountains quartzite) $\delta^{18}O$ and U-Pb isotopic age are correlated using in situ analyses from the same crystal by ion microprobe. U-Pb age was measured from 20 to 30 μm spots (<1 ng) by SHRIMP II at Curtin University (Wilde et al. 2001; Peck et al. 2001) or at the Chinese Academy of Geological Sciences (Cavosie et al. 2004). For samples with multiple spots, the oldest concordant age is reported. Two generations of oxygen isotope data are reported. In 1999, $\delta^{18}O$ was measured by CAMECA ims-4f using a 10 kV beam of $^{133}Cs^+$, high energy offset (14.15 kV total potential), and a single electron multiplier at the University of Edinburgh (precision ~ 1.0‰, 1 SD, Peck et al. 2001). In 2004, $\delta^{18}O$ was measured at the University of Edinburgh by CAMECA ims-1270 using high mass-resolution and dual faraday detectors (precision ~ 0.3‰, 1 SD, Cavosie et al. 2005). A careful protocol for analysis is documented in each study where standard analyses bracket unknowns and represent 25–50% of all analyses in each analytical session. The analytical pits for oxygen isotope analyses made in 2004 are, when possible, directly below the polished locations of age measurements and were examined after analysis by SEM. No artifacts of earlier analyses were detected, but cracks and inclusions can be evaluated. These ion microprobe data represent sample sizes that are 10^6 times smaller (ng vs. mg) than the laser fluorination data. Most crystals are homogeneous in $\delta^{18}O$ within analytical uncertainty and the average value is reported for single crystals where multiple analyses were made.

Results

Archean

Zircon concentrates were analyzed for $\delta^{18}O$ from 121 Archean rocks from four geologic provinces on three continents (Fig. 2, Table 1, Appendix 1). In addition, 67 detrital igneous zircons were analyzed by ion microprobe. The igneous Archean zircons have a small range of

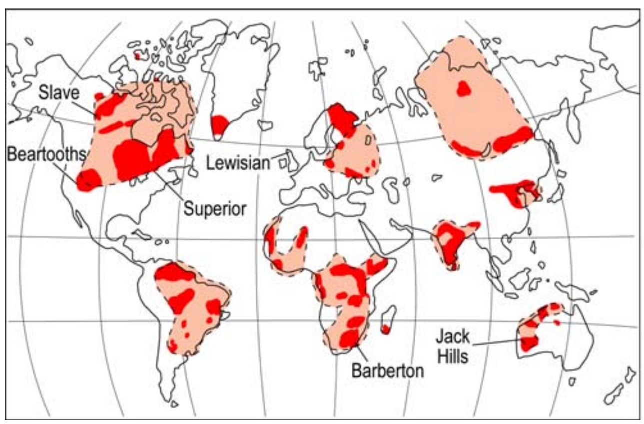

Fig. 2 Map showing the exposed and inferred extent of Archean rocks and areas studied (from Peck and Valley 2005)

δ^{18}O (5.0–7.4‰). Taken together, the data yield an average of δ^{18}O(Zrc) = 5.82 ±0.74‰ (Fig. 3a) and no variability is seen with age or SiO_2 content throughout the period 4.4–2.5 Ga (Figs. 4 and 5). However, even within this limited range of values, there are correlations with the host rock type. Most samples have primitive δ^{18}O(Zrc) values (5.5 ± 0.7‰) that would be expected for igneous rocks differentiated directly from the mantle, or remelted or equilibrated at high temperatures with such rocks (5.3 ± 0.3‰, Valley et al. 1998). A distinct subset, described below, has higher values up to 7.4‰.

Jack Hills

The Jack Hills are in the Narryer gneiss terrane, NW Yilgarn craton, Western Australia. Conglomerates and quartzites contain detrital zircons and have experienced upper greenschist to amphibolite facies metamorphism. The values reported in Appendix 1 are the average δ^{18}O for each of 57 detrital zircons from four samples of the Jack Hills metaconglomerate and quartzite, including sample W-74 that was previously known to contain zircons with ages from 4.4 to < 3.1 Ga (Compston and Pidgeon 1986; Wilde et al. 2001). These zircons are interpreted as igneous based on fine concentric or sector zoning imaged by cathodoluminescence. Some zircons contain inclusions of quartz and devitrified melt. The ages that are less than 3.73 Ga match the known crystallization history of granitic rocks and gneisses that outcrop adjacent to the Jack Hills. However, no rocks are known that are old enough to be the source of zircons older than 4 Ga. Several zircons have now been found older than 4.3 Ga, which are the oldest known terrestrial samples (Wilde et al. 2001; Cavosie et al. 2004; unpublished data). The δ^{18}O values in Appendix 1 represent averages of up to 12 independent spot analyses on a single zircon (Peck et al. 2001; Cavosie et al. 2005). The analytical precision on a single ion microprobe spot (20 μm dia.) in 2004 is ±0.2–0.6‰ (1 SD). The uncertainty of the mean improves to ±0.1–0.2‰ for ten replicate analyses in a homogeneous crystal.

These in situ ion microprobe analyses provide unique information on intra- and inter-crystal variation that is essential for correlation of δ^{18}O and age. However, ion microprobe analysis of δ^{18}O in detrital zircons is a difficult and relatively new technique. The only tabulated data published for critical evaluation come from two studies that show CL images and describe a careful protocol for analysis that is required for accurate standardization (Peck et al. 2001; Cavosie et al. 2005). As a further test of accuracy, we compare the average δ^{18}O of all Jack Hills zircons in Appendix 1 (δ^{18}O(Zrc) = 6.2 ± 0.7‰, range = 5.0–7.4‰) to the δ^{18}O measured by more accurate and precise laser fluorination for a bulk sample of several hundred Jack Hills zircons (6.3 ± 0.1‰, Peck et al. 2001). These average values are identical within analytical uncertainty to each other and the range for Jack Hills zircons is the same as for all other Archean igneous zircons that have been analyzed.

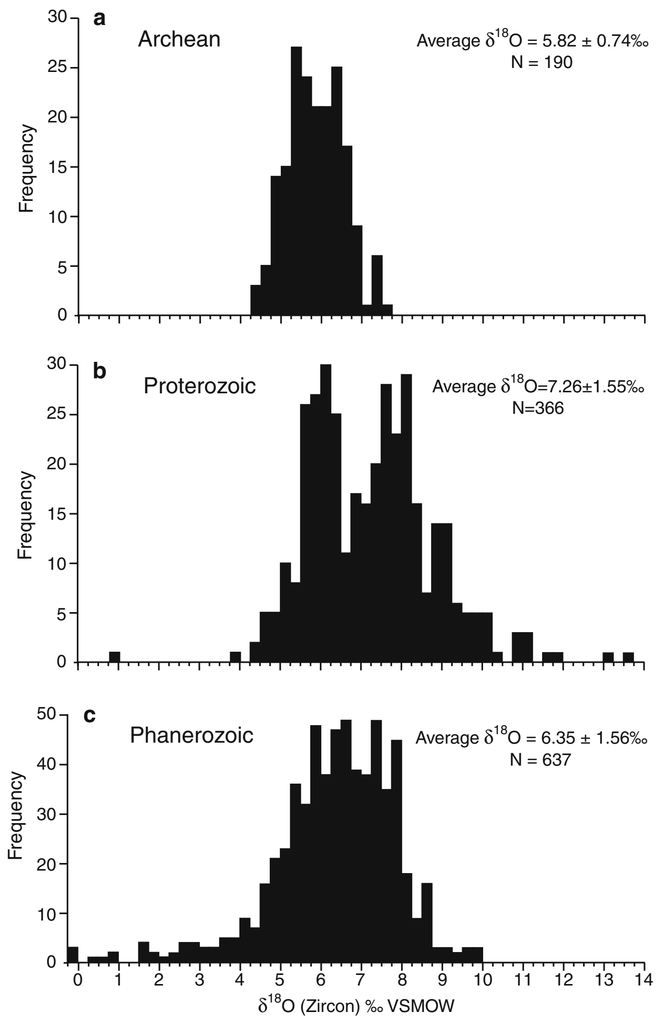

Fig. 3 Histograms of δ^{18}O(Zrc) for igneous zircons: **a** Archean; **b** Proterozoic; **c** Phanerozoic

Higher values of δ^{18}O from 7 to 15‰ have been reported for ion microprobe analyses of at least 15 pre-4 Ga zircons from the Jack Hills (Mojzsis et al. 2001; Trail et al. 2005), but neither the data tables nor images necessary for interpretation of this unusual result are published yet. These analyses are not included in Fig. 4. If magmatic, values above 7.5‰ would be in contrast to the Archean results summarized here (see discussion in Peck et al. 2001; Cavosie et al. 2005). Cavosie et al. (2005) report one 3.9 Ga zircon with δ^{18}O = 10.3, which is interpreted as altered based on crosscutting textures seen in CL (their Fig. 7). Because of the complexity seen in CL images of some zircons and the difficulty of stable isotope analysis by ion microprobe, such results require detailed documentation.

Beartooth Mountains

Ten zircons were analyzed for δ^{18}O by ion microprobe from the Beartooth Mountains, Montana in the

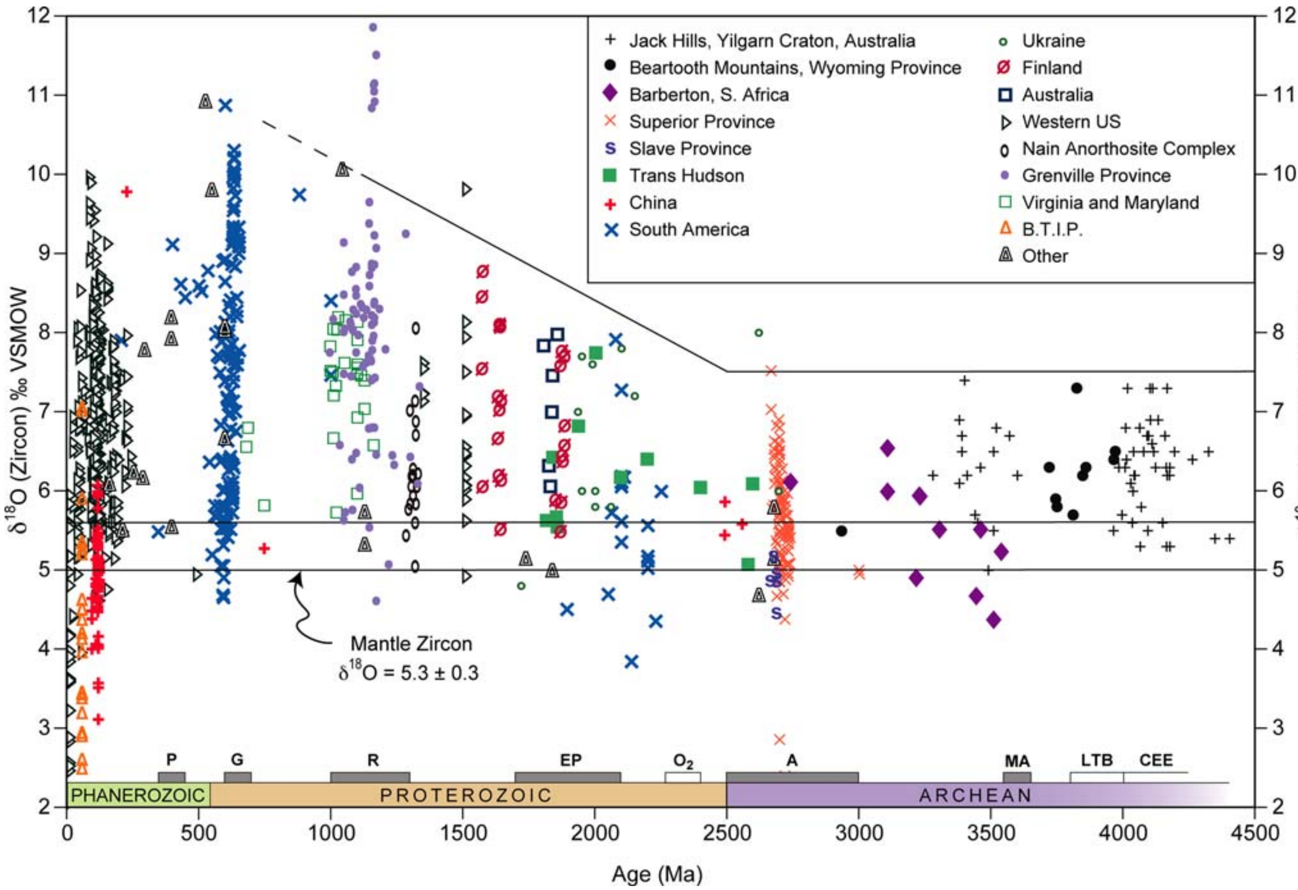

Fig. 4 Compilation of $\delta^{18}O(Zrc)$ versus age for zircons from 1,200 rocks with known age. Samples range in age from 4.4 Ga to 0.2 Ma and come from many terranes on seven continents. A remarkable uniformity is seen in the Archean, values cluster near the mantle ($\delta^{18}O(Zrc) = 5.3 \pm 0.3‰$) with some values as high as 7.5‰ (horizontal line) due to recycling of supracrustal material into magmas. Higher $\delta^{18}O$, above 7.5‰, only occurs after 2.5 Ga, reflecting intra-crustal recycling of high $\delta^{18}O$ material and maturation of the crust. Oxygen isotope data are from Table 1 and Appendix 1. Periods of supercontinent growth are shown by *short bars* at *bottom*: *P* Pangea; *G* Gondwana; *R* Rodinia, *EP* Early Proterozoic; *A* Archean; and *MA* Middle Archean (Condie 1998). *LTB* Late Terminal bombardment, *CEE* Cool Early Earth (Valley et al. 2002), and O_2 = rise of oxygen in the atmosphere

Archean Wyoming Province. These detrital zircons are from quartzites in the same area of Hell Roaring Plateau where Mueller et al. (1992, 1998) reported SHRIMP ages as old as 4.0 Ga. Our new SHRIMP data confirm this age distribution and nine zircons between 4.0 and 3.7 Ga were analyzed for $\delta^{18}O$. The values of $\delta^{18}O$ average $6.2 \pm 0.5‰$ and range from 5.5 to 7.3‰, nearly identical to the older detrital zircons from the Jack Hills.

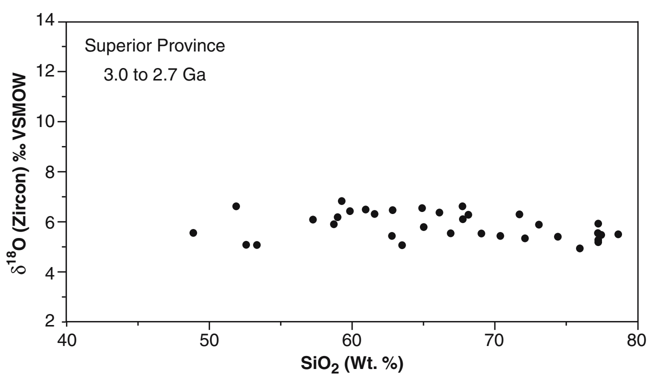

Fig. 5 Plot of $\delta^{18}O(Zrc)$ versus SiO_2 content for magmatic zircons and their host rocks for 35 samples from the Archean Superior Province, Canada. Most samples are tonalites, trondhjemites and granodiorites (*TTG*) or associated volcanic rocks and average $\delta^{18}O = 5.5 \pm 0.7‰$ (1 SD). High-Mg sanukitoids have mild enrichments in $^{18}O/^{16}O$, averaging $6.5 \pm 0.4‰$

Barberton

Zircons were analyzed from 11 rocks from Barberton, South Africa (3.5–2.7 Ga). The samples average $\delta^{18}O(Zrc) = 5.5 \pm 0.7‰$ (King 2001). These are the oldest zircons that have been analyzed by high precision laser fluorination. The values are indistinguishable from the younger Superior Province samples.

Superior Province

The largest set of Archean $\delta^{18}O(Zrc)$ data comes from 58 plutonic rocks and 44 volcanic rocks of the Superior Province of Canada (3.0–2.7 Ga). These samples are representative of over 100,000 km^2 within the southern and western Superior Province (Fig. 6). Of the plutonic rocks, 42 are pretectonic to syntectonic, mostly tonalite-trondhjemite-granodiorite (TTG) and $\delta^{18}O$ averages $5.6 \pm 0.5‰$ (1SD, Fig. 7, King et al. 1998; King 2001). Volcanic zircons yield the same values, $\delta^{18}O(Zrc) = 5.4 \pm 0.8‰$ (King et al. 1997; 2000; King 1997). In contrast, higher $\delta^{18}O$ values of $6.5 \pm 0.4‰$ ($n = 17$) come from late tectonic to post-tectonic (2.70–2.68 Ga), Mg- and LREE-enriched plutons with sanukitoid affinities (King et al. 1998). These mildly elevated values support the model that sanukitoids formed during subduction by melting of altered upper ocean crust and/or peridotite in the overlying mantle wedge that was metasomatized by fluids from ocean crust (Shirey and Hanson 1984; Stern and Hanson 1991). The upper portion of ocean crust is elevated in $^{18}O/^{16}O$ due to low temperature hydrothermal alteration and the presence of high $\delta^{18}O$ sediments, and thus metasomatizing fluids are likewise high in $\delta^{18}O$ (Eiler et al. 1998; Eiler 2001). Some TTG plutons from metasedimentary belts also show mildly higher $\delta^{18}O$. For instance, three plutons from the metasediment-rich English River subprovince have $\delta^{18}O(Zrc) = 6.6 \pm 0.2‰$ recording crustal contamination (King et al. 1998).

Other rocks of the same age, 3.0–2.7 Ga, have similar values including: two samples of tonalitic gneiss from the Lewisian of Scotland ($\delta^{18}O(Zrc) = 5.5$), five samples from the Slave province, Canada ($\delta^{18}O = 4.9 \pm 0.3‰$, King et al. 2001), and two samples from the Ukraine that were analyzed in conventional nickel reaction vessels (Lugovaya et al. 2001).

There are three Archean low $\delta^{18}O$ outliers in Fig. 4 at ~2.7 Ga that are from volcanic rocks. Two samples were collected from cordierite-orthoamphibole metavolcanics in the stockwork zone of the Manitouage volcanogenic massive sulfide deposits at Geco, Ontario. In this environment, low $\delta^{18}O$ values are common due to the high temperature alteration of basalt by seawater, which formed the Mg-Al-rich protoliths to cordierite gneisses (Pan and Fleet 1995). The low $\delta^{18}O$ values of igneous zircons (2.4 and 4.4‰) show that these low $\delta^{18}O$ protoliths were remelted (Peck 2000). The third low $\delta^{18}O$ zircon (2.9‰) is from rhyolite at Winston Lake and is explained by remelting of altered rocks in the Sturgeon Lake caldera complex (King et al. 2000).

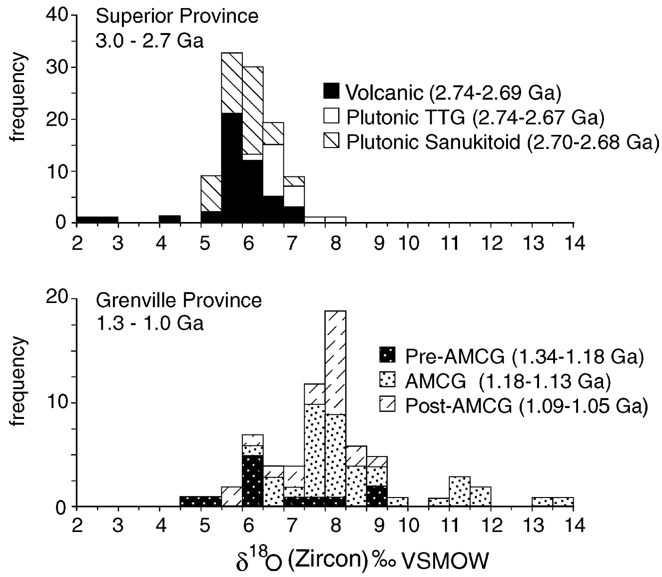

Fig. 7 Histograms of $\delta^{18}O$ for igneous zircons from the Superior and Grenville Provinces (after Peck et al. 2000)

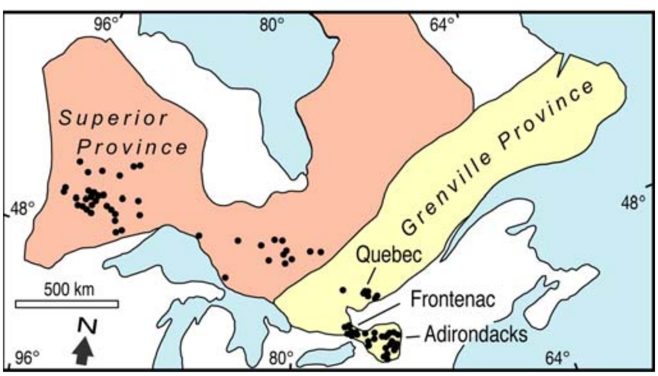

Fig. 6 Map of the Superior and Grenville Provinces of North America showing sample localities (after Peck et al. 2000)

Proterozoic

The $\delta^{18}O$ for zircons from a total of 366 Proterozoic rocks range from 1 to 13‰ (average $7.3 \pm 1.5‰$). This average is 1.4‰ higher than for all of the Archean samples and the range is two to three times larger (Fig. 3b vs. 3a). The values are bimodal. Similar differences (Fig. 7) were reported earlier for zircons from the Grenville Province vs. the Superior Province (Peck et al. 2000). It is now clear that this evolution from uniform $\delta^{18}O(Zrc)$ values (~5 to 7.5‰) in the Archean to more variable and higher values (~5 to >10‰) in the Proterozoic occurs worldwide and is not restricted to N. America.

Grenville Province

The most heavily studied and most variable Proterozoic samples are from the Grenville Province (ca. 1.35–1.0 Ga: Adirondacks, NY; Ontario including the Frontenac terrane; and Quebec; Valley et al. 1994; Peck et al. 2004), and Grenville outliers in Vermont, the Blue Ridge, Goochland regions of Virginia, and the Baltimore Gneiss of Maryland. The zircons from 107 rocks vary from 4.6 to 13.5‰ and average $7.9 \pm 1.6‰$ (one sample from a pegmatite intruding low $\delta^{18}O$ skarn is 1.0‰).

Figure 8 shows the ages and $\delta^{18}O$ values for the Grenville Province. A major magmatic event, the ca.

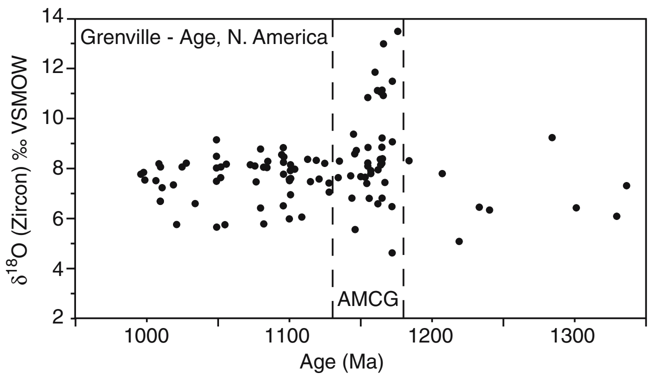

Fig. 8 Plot of δ^{18}O(Zrc) versus age for magmatic zircons from the Grenville Province. High δ^{18}O rocks from the Frontenac Arch with δ^{18}O > 10‰ formed during the AMCG magmatism at 1,180–1,130 Ma (*vertical dashed lines*)

1.15 Ga AMCG suite (anorthosite–mangerite–charnockite–granite), is seen for plutons from the Adirondacks and southern Grenville. Figure 7 shows δ^{18}O for zircons from Grenville plutons: pre-AMCG (1.34–1.18 Ga), AMCG (1.18–1.13 Ga), and post-AMCG (1.09–1.05 Ga) (Peck et al. 2000, 2004).

Figure 9 shows the Grenville-age δ^{18}O(Zrc) values versus whole rock SiO_2. The majority of samples fall between 6 and 10‰ and δ^{18}O shows no correlation with SiO_2, which varies from 41 to 77 wt.%. This range of δ^{18}O values is representative of the entire southern Grenville province and is higher than seen in Archean samples.

A group of eight samples have unusually high δ^{18}O(Zrc) of ~11 to 13‰, corresponding to the spike at ~1.15 Ga in Figs. 4 and 8. These samples are from a relatively small group of AMCG-age plutons in the Frontenac arch and NW Adirondack Lowlands between Ontario and the central Adirondack Highlands, NY. Silica varies from 61 to 75 wt % for these rocks (Fig. 9). The Frontenac granites were first identified as high in δ^{18}O by Shieh (1985) from whole rock data and have

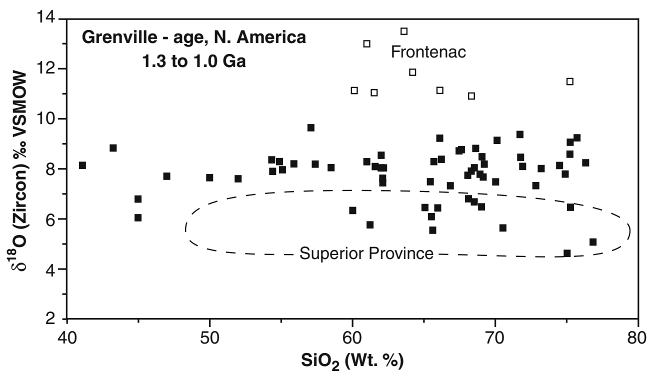

Fig. 9 Plot of δ^{18}O for magmatic zircons versus SiO_2 content of their host rocks for 75 samples from the Grenville Province. Frontenac samples are shown as open boxes. The field for Superior Province samples is shown for comparison from Fig. 5

been intensely studied because of their unusual oxygen isotope ratio (Marcantonio et al. 1990; Peck et al. 2004). The new zircon analyses show that these high δ^{18}O zircons crystallized from high δ^{18}O magmas and are not the result of postmagmatic alteration. These are the highest δ^{18}O igneous zircons that have been reported and their compositions are anomalous in Figs. 3b, 4, 7, 8, and 9. Such magmas must result from melting of sediments and/or altered ocean crust, which were buried deeply, probably during continent–continent collision at ca. 1.2 Ga (Peck et al. 2004). The unusually high values (δ^{18}O(Zrc) > 10‰) are only seen in the post-Elzevirian AMCG suite. Regardless of their genesis, the number of analyses of these rocks over-represents their volume in the crust. The majority of Grenville crust is represented by values of δ^{18}O(Zrc) from 6.0 to 9.5‰. The values for Superior Province zircons (Fig. 5) are outlined in Fig. 9 emphasizing the contrast in δ^{18}O between these adjacent terranes.

The Grenville-age samples (1.1–1.0 Ga) from Virginia (Blue Ridge, Goochland) and Maryland (Baltimore Gneiss) are less variable in δ^{18}O than the samples from the Adirondacks of New York and adjacent terranes in Ontario but still are significantly higher (average 7.4‰) than in the Archean.

Finland

Oxygen isotope ratios of igneous zircons from granitoids that intrude the Svecofennian of Finland also reveal discontinuities in the deep crust. Three magmatic source regions with distinct oxygen and neodymium isotope signatures are revealed in a north–south traverse. Zircons from the 1.88–1.87 Ga Central Finland Granitoid Complex (CFGC) range from 5.5 to 6.8‰ ($n = 7$), except for three plutons in contact with supracrustal belts. South of the CFGC, zircon from 1.65 to 1.54 Ga rapakivi granites average 8.1 ± 0.6‰ ($n = 5$). Lastly, zircons from 1.65 to 1.54 Ga granites in southernmost Finland average 6.1 ± 0.1‰ ($n = 3$). These three magmatic source regions are interpreted to reflect differences in accreted Paleoproterozoic island arc terrains (Elliott et al. 2005).

South America

Zircons from Proterozoic rocks in South America were analyzed from Brazil and Uruguay. Ages fall into two groups: 2.36–1.70 Ga and 653–560 Ma. Early Proterozoic samples are from the Ribeira belt, the Curitiba microplate, Luis Alves microplate, SE border of San Francisco craton, Caldas Brandão massif, and the Piedra Alta terrane. Late Proterozoic samples are from NE Parana State, Paranaguá and Monguaguá batholiths, Serra do Mar Alkaline-Peralkaline suite, Pien batholith, Florianópolis batholith, Pelotas batholith, Sao Rafael pluton, Serido terrane, Emas pluton, Cachoeirinha terrane, Aigua batholith, and the Lavalleja metamorphic complex. Data for these samples are reported in Table 1 and Appendix 1 (Ferreira et al. 2003). Appendix 2 shows $\delta^{18}O$(Zrc) versus wt.% SiO_2 for the Late Proterozoic rocks from Brazil. As for other suites, there is no correlation of $\delta^{18}O$ and SiO_2.

Neoproterozoic

The Late Proterozoic plutons that intrude the Grenville-age rocks in the Blue Ridge of Virginia have a measurably lower average $\delta^{18}O$ than nearby Grenville-age plutons (average 6.4 vs. 7.4‰) and suggest addition of juvenile magmas within an evolved high $\delta^{18}O$ province.

Other Terranes

Zircons from smaller suites of Proterozoic samples were analyzed from: northern Australia; basement in the Basin and Range, western US.; Trans-Hudson, Canada; Nain Anorthosite Complex, Canada; Laramie anorthosite complex, Wyoming (O'Connor and Morrison 1999); Ukraine (Lugovaya et al. 2001); and Penokean of Wisconsin. The ages, values of $\delta^{18}O$, and references for these samples are summarized in Table 1 and tabulated in Appendix 1.

Phanerozoic

Sierra Nevada

The Sierra Nevada batholith, USA, is dominated by Cretaceous plutons intruded into predominantly Jurassic and Triassic granitoids, metasediments, and metavolcanics. Zircons have been analyzed for $\delta^{18}O$ from 287 rocks varying in age from 143 to 74 Ma, and 40 rocks from 222 to 145 Ma (Lackey 2005; Lackey et al. 2005a, b). Values of $\delta^{18}O$(Zrc) are highly variable with no significant difference between Cretaceous and Jurassic/Triassic plutons (7.0 ± 0.9‰ and 6.7 ± 0.7‰, respectively).

Consistent differences in $\delta^{18}O$ are seen correlating to location within the batholith, rock type, and depth of emplacement. The highest $\delta^{18}O$ zircons are from 35 samples from peraluminous garnet-bearing plutons, which average 7.9 ± 0.5‰ (Lackey et al. 2005b). If the peraluminous rocks are not included, the difference between Cretaceous and older granitoids is not significant (6.8 ± 0.8‰ vs. 6.7 ± 0.7‰). However, distinct geographic differences persist between the eastern, southern, and northern Sierra, and other areas (t-test at greater than 99% confidence level): western Sierra, 6.8 ± 0.8‰ n = 36; central Sierra, 6.9 ± 0.6‰ n = 91; eastern Sierra, 6.2 ± 0.5‰ n = 85; Owens Valley/ White Mountains, 6.8 ± 0.7 n = 31; and northern Sierra, 5.5 ± 0.6‰ n = 3 (Table 1). While most of the Sierra Nevada batholith presently exposes rocks that intruded at depths of 5–13 km, the southernmost Sierra (Tehachapi Mountains) intruded at 20–30 km and represent deeper levels of the batholith. Zircons from the southern Sierra are the highest from metaluminous gabbro, diorite, and tonalite plutons, and average 7.8 ± 0.7‰ (n = 45), reflecting melting of metasedimentary rocks.

It is intriguing in the Sierra Nevada that $\delta^{18}O$(Zrc) and initial $^{87}Sr/^{86}Sr$ values have a negative correlation over much of the batholith, and that lower values of $\delta^{18}O$(Zrc) are found in the east, towards the craton. In fact, some of the highest $\delta^{18}O$(Zrc) values are from rocks with Sr_i less than 0.706. The opposite relation is predicted for a west to east transition of oceanic to continental crust or for AFC processes involving high $\delta^{18}O$ sediments. The adjacent Peninsula Ranges batholith shows the predicted trends (Taylor 1986), in distinct contrast to the Sierras. The negative correlation of $\delta^{18}O$ and Sr_i is evidence in the Sierras for considerable recycling of young (Paleozoic or Mesozoic), hydrothermally altered upper oceanic crust or volcanic arc sediments within the arc (Lackey et al. 2005a; Lackey 2005). The occurrence of lower average $\delta^{18}O$ in granitoids of the eastern Sierra, on the cratonic side of the arc, indicates that magmas there were derived from aged lithospheric mantle and were not significantly contaminated by overlying craton-derived sediments (Lackey 2005).

Great Basin, Western US

Zircons have been analyzed from 124 Jurassic to Tertiary granitic rocks from the Great Basin of Nevada and Utah (King et al. 2004). Samples span mapped isopleths for $^{87}Sr/^{86}Sr_i$ = 0.708 and 0.706, and ϵNd = −7. Zircons of all ages show an increase in $\delta^{18}O$ to the east of the 0.706 line, correlating with increased ratios of whole rock $Al_2O_3/(CaO + Na_2O + K_2O)$. The crustal boundaries defined by radiogenic isotopes in the Great Basin agree with discontinuities in $\delta^{18}O$(Zrc) in contrast to whole rock $\delta^{18}O$ values, which are frequently altered and correlate poorly.

Idaho Batholith

The late Cretaceous and Tertiary granitic rocks of the Idaho batholith intruded the Precambrian margin of North America. Values of $\delta^{18}O$(Zrc) are relatively homogeneous in spite of prolonged magmatic history. Zircons in the Bitterroot Lobe (northern part of batholith) average 7.1 ± 0.3‰ (n = 7), while in the Atlanta Lobe (southern), they average 6.7 ± 1.5‰ (n = 19). Eocene plutons average 7.2 ± 0.2‰ (n = 3) with one exception at 4.0‰ (King and Valley 2001).

Eastern China

A-type granites from four late-Mesozoic plutons in eastern China have an average $\delta^{18}O$(Zrc) = 4.9 ± 0.3‰

($n=30$), while a fifth pluton averages $\delta^{18}O(Zrc)$ = 3.7 ±0.4‰ ($n=6$) (Wei et al. 2002; unpublished). These mildly low $\delta^{18}O$ magmas suggest protoliths or magmatic contaminants that exchanged with surface waters at high temperature.

British Tertiary Igneous Province

Sub-volcanic igneous centers have been studied from the Isles of Skye, Arran, and Mull in Scotland demonstrating the presence of low $\delta^{18}O$ values as a result of magmatic and post-magmatic processes typically localized within eroded caldera complexes. In spite of extreme hydrothermal alteration of many rocks, all evidence indicates that low $\delta^{18}O$ values in zircon are magmatic compositions. In many cases, the low $\delta^{18}O$ magmas resulted from cannibalization, i.e., remelting of hydrothermally altered earlier phases of the same igneous suite (see, Valley 2003). The resulting $\delta^{18}O(Zrc)$ values range from 0.6 to 7.1‰ ($n=27$, Gilliam and Valley 1997; Monani and Valley 2001).

Tertiary volcanic rocks, Western US

Volcanic rocks have been studied in detail from caldera complexes at Yellowstone, Long Valley, and Timber Mountain/Oasis Valley in the western United States. Relatively small volume, postcaldera rhyolites at Yellowstone have low $\delta^{18}O(Zrc)$ values to 0.0‰, in comparison to the large (600–2,500 km^3) caldera forming Huckleberry Ridge and Lava Creek tuffs ($\delta^{18}O(Zrc)$ = 4.1–5.7‰, Bindeman and Valley 2000, 2001). Low $\delta^{18}O$ rhyolites are also found at the Timber Mountain/ Oasis Valley Caldera complex in Nevada where smaller depletions of 1–2‰ are seen, but the volumes of low $\delta^{18}O$ rock are significantly larger for the Tiva Canyon and Ammonia Tanks tuffs (900–1,000 km^3, Bindeman and Valley 2003). In contrast to these nested caldera complexes, zircons from the Bishop tuff (>650 km^3) at Long Valley caldera are mantle-like and homogeneous in $\delta^{18}O$ (5.8 ±0.2‰, $n=4$, Bindeman and Valley 2002).

Mantle zircons

Zircon megacrysts are a trace constituent in many kimberlites. Typically, the U-Pb age matches the eruption age of the kimberlite pipe, and the $\delta^{18}O$ of zircons approximates high temperature equilibration with the mantle ($\delta^{18}O(Zrc) = 5.3 \pm 0.3$‰). This value would be in magmatic equilibrium with an oceanic basalt at $\delta^{18}O(WR)$ = 5.5‰ and is the predicted value of $\delta^{18}O$ in primitive mantle-derived magmas. While $\delta^{18}O$ is very homogeneous for zircons from each pipe, within less than ±0.2‰, small regional variability is observed with some pipes having values either above or below the mantle value (Valley et al. 1998; unpublished data). Ion microprobe analysis of a few selected crystals, including KIM-4 and KIM-5 standards, has shown intra-crystalline homogeneity (Peck et al. 2001; Valley 2003; Cavosie et al. 2005). Precambrian zircons from Zwaneng, Botswana are anomalous and show inter- and intra-crystalline variability (Valley et al. 1998; Valley and McKeegan unpublished), consistent with a prolonged history in the crust. The kimberlite zircons are a distinct suite with clear mantle affinities and will not be considered further in this paper, which addresses the maturation of continental crust.

A Secular Change in magmatic $\delta^{18}O$

Figure 4 shows a secular change in $\delta^{18}O(Zrc)$. Zircons from younger magmas are more variable and many are higher in $\delta^{18}O$. The large amount of information in Fig. 4 complicates the simple trend and has been replotted in Fig. 10a where all data have the same symbol. This figure emphasizes that values were relatively low and constant throughout the Archean, and shows that the trend towards increasing values began at ~2.5 Ga. A horizontal line at $\delta^{18}O$ = 7.5‰ defines the highest values in the Archean. After 2.5 Ga, the upper limit of $\delta^{18}O(Zrc)$ increases to 10‰ at ca. 1 Ga, encompassing all data except the anomalous Frontenac samples at 1.15 Ga. While it might be tempting to fit a more complex curve to these data with peaks and valleys, the valleys fall in intervals with less data and probably result from the statistics of small populations.

The interpretation of the trend in Fig. 4 depends critically on the conclusion that all values are faithfully preserved from the original magma. Apparent secular trends of $\delta^{18}O$ in carbonates and cherts have been attributed by some to problems of preservation, where the oldest samples are interpreted to be most altered. There are two reasons why the trend in Figs. 4 and 10a cannot be dismissed as the result of postmagmatic disturbance. First, all evidence indicates that crystalline zircons reliably preserve their magmatic value of $\delta^{18}O$, and second, there is no reason why alteration would affect only the youngest rocks. Disturbance of $\delta^{18}O$ would be expected to be greater on average in older rocks, which have had more opportunity to experience metamorphism, radiation damage, and other forms of alteration. Clearly, the trend in Figs. 4 and 10a is the opposite of that expected if older samples are more altered.

It is important to emphasize that there are no known primitive reservoirs in the mantle for the extreme $\delta^{18}O(Zrc)$ values of Fig. 4 (e.g., >6.0‰ or <4.6‰).

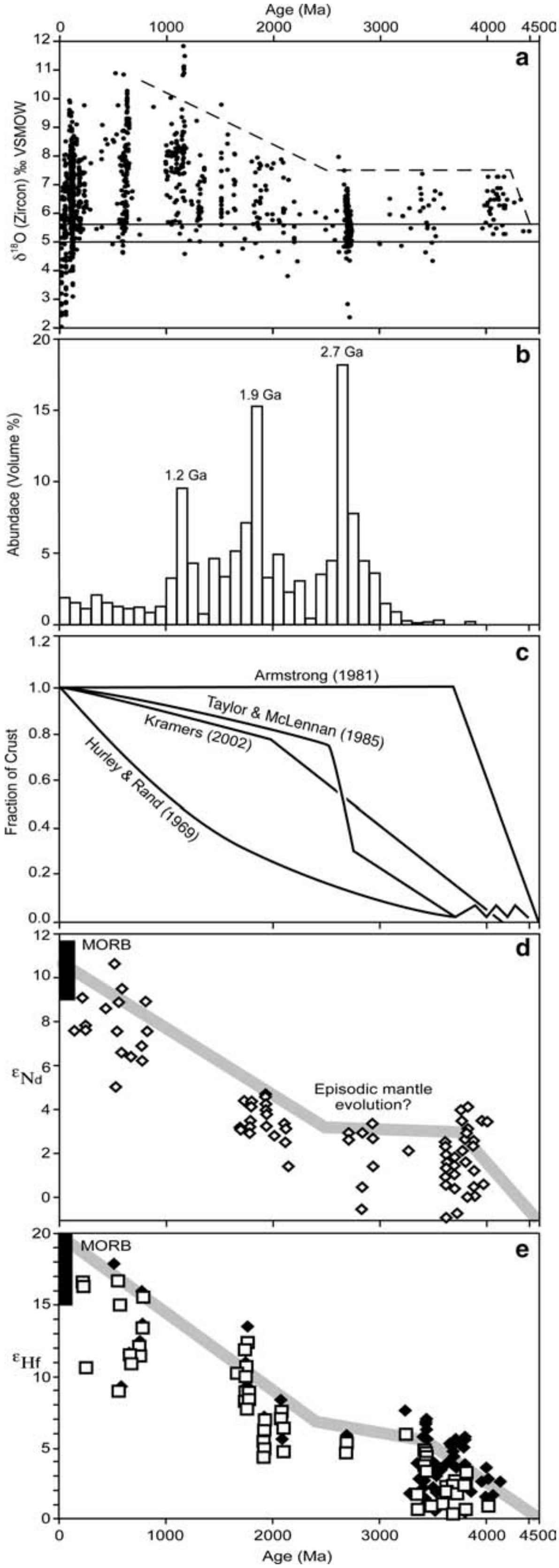

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Fig. 10 Mantle evolution and crustal growth, and maturation are shown by stable and radiogenic isotopes. **a**. Values of δ^{18}O(Zrc) and age of igneous zircons (Fig. 4). **b**. Distribution of zircon ages from juvenile crust (Condie 1998). **10c**. Crustal growth curves representative of many that have been proposed based on the preserved rock record and a simplified line from Kramers (2002). **d and e**. Evolution of the depleted mantle as shown by Nd and Hf isotopes compiled by Bennett (2003) who infers a rapid period of early fractionation followed by steady state through much of the Archean and major fractionation after 2.5 Ga

Fractionations are small at high temperatures and thus formation of δ^{18}O values higher or lower than the mantle requires protoliths that were altered near the surface of the Earth where temperatures are low and fractionations are large. Where anomalous δ^{18}O values have been identified in the mantle, they represent subducted supracrustal material.

Thus, the variability of δ^{18}O(Zrc) is a sensitive record of recycling of supracrustal lithologies. Figure 1 shows that reasonable supracrustal contaminants range in δ^{18}O to values above 25‰. Even small amounts of such near-surface rocks would cause a measurable increase in δ^{18}O of magmas and zircons. For instance, 5% contamination by a rock with δ^{18}O = 25‰ would raise δ^{18}O in a normal magma by ~1‰. Likewise, bulk melting of igneous rocks mixed with 5% metasediments could raise δ^{18}O by 1‰. Thus, while questions remain about timing and cause, it is apparent that processes of intracrustal recycling have systematically changed the amounts of contamination and melting through time and/or the δ^{18}O of fertile crust has increased through time.

High δ^{18}O magmas

Values of δ^{18}O(Zrc) above 7.5‰ are common in magmas younger than 1.5 Ga. These high δ^{18}O zircons are representative of rocks outcropping over large areas of several terranes, including: the southern Grenville Province (1.34–1.05 Ga, Fig. 7); Grenville-age outliers in the Appalachians; several regions of South America (Emas and Tavares plutons, ~650 Ma); and the Sierra Nevada batholith (222–74 Ma). Smaller proportions of other terranes have high δ^{18}O igneous compositions including: the Ukrainian shield (2.62–1.93 Ga); Australia (1.86–1.80 Ga); Finland (1.88–1.57 Ga); the Great Basin (1.5 Ga); and the Idaho batholith (94–70 Ma). With the exception of the Frontenac AMCG suite and garnet-bearing peraluminous granitoids of the Sierra Nevada batholith, these high δ^{18}O rocks were not targeted for special study. Thus, the proportion of high δ^{18}O zircons in Appendix 1 is the best estimate available for the proportion of high δ^{18}O igneous rocks in these areas.

The high δ^{18}O(Zrc) values are in contrast to the Archean when values are lower, close to the δ^{18}O(Zrc) values expected in mantle-derived (4.6–6‰) or mildly evolved (6–7.5‰) magmas. Zircons from 7.5–10‰ indicate high δ^{18}O whole rock values of 9 to 12‰ for felsic magmas, consistent with derivation by melting of sediments as is observed in "S-type" granites (Fig. 1, O'Neil and Chappell 1977; O'Neil et al. 1977; Taylor and Sheppard 1986). However, many of the host rocks for these high $\delta^{18}O$ zircons are not peraluminous and major element chemistry is not a good predictor for high $\delta^{18}O$ magmas in the absence of other evidence. Low temperature alteration is a common mechanism that can raise the $\delta^{18}O$ of near-surface rocks without necessarily changing other chemical characteristics. Thus, it is likely that assimilants other than high-Al clays are important and that oxygen isotope behavior is variably decoupled from other geochemical systems.

The number of high $\delta^{18}O$(Zrc) samples increases gradually over a period of approximately one billion years during the Proterozoic (Figs. 4, 10a). The one exception to a smooth trend is the anomalous group of high $\delta^{18}O$ Frontenac samples. The transition from lower to higher $\delta^{18}O$ starts at approximately the end of the Archean, but the exact timing is poorly constrained due to limited samples between 2.7 and 2.0 Ga.

This secular change in oxygen isotopic reservoir characteristics marks a major non-uniformitarian transition in the Earth's continental crust. Higher $\delta^{18}O$ values result from subduction or burial of high-$\delta^{18}O$ sediments, and rocks weathered or altered at low temperatures, which are then recycled in high $\delta^{18}O$ magmas. Clearly, such high $\delta^{18}O$ rocks have been increasingly recycled within the crust starting in the Proterozoic.

Low $\delta^{18}O$ magmas

Young samples with $\delta^{18}O < 5‰$ are common in Fig. 4 for the past 150 Ma, but only a few scattered samples are seen from older rocks. A few values in this time period are as low as 0‰. These data are tabulated in Appendix 1, but values below 2.3‰ are not shown in Fig. 4 to save space. It is reasonable to ask if the concentration of values that are lower than the mantle also represent a secular change in magmatic $\delta^{18}O$. The low $\delta^{18}O$ samples represent three relatively small areas that were chosen for close examination specifically because previous studies suggested the presence of low $\delta^{18}O$ magmas: sub-volcanic granites from the British Tertiary Igneous Province (Gilliam and Valley 1997; Monani and Valley 2001) and eastern China (Wei et al. 2002; unpublished); and low-$\delta^{18}O$ rhyolites from Yellowstone (Bindeman and Valley 2001, 2002). These three areas represent shallow sub-volcanic magma chambers where low $\delta^{18}O$ values resulted from melting of hydrothermally altered wall rock. In the course of investigations of the genesis of low $\delta^{18}O$ magmas, the lowest $\delta^{18}O$ rocks from each area were intensely collected and studied, biasing the proportions of analyses in Figs. 3c and 4. For instance, at Yellowstone, the largest caldera-forming eruption, Huckleberry Ridge tuff was 2,500 km^3 in volume and the low $\delta^{18}O$ rhyolites represent intra-caldera flows of 10–50 km^3 each (Hildreth et al. 1984), yet the number of analyses for low $\delta^{18}O$ rhyolites exceeds that for the caldera-forming eruptions. Thus, the volume of low $\delta^{18}O$ magmas is significantly over represented by the number of analyses in Figs. 3c and 4.

Extremely low $\delta^{18}O$ zircons (to $-11‰$) of igneous origin are reported from the Dabie-Sulu terrane, China (Rumble et al. 2002; Chen et al. 2003; Zheng et al. 2004; Zhao et al. 2004). These zircons have been intensely studied because host rocks include coesite- and diamond-bearing eclogites. Igneous ages are ~0.8 to 0.7 Ga, 0.5 Ga older than ultrahigh pressure metamorphism. The low $\delta^{18}O$ values are attributed to high temperature exchange with very low $\delta^{18}O$ glacial melt-water during Snowball Earth events in the Neoproterozoic (Rumble et al. 2002; Zheng et al. 2004). No other zircons below ~0‰ have been reported and these unusual values may be unique. They are not plotted in Fig. 4 for simplification.

The question persists; why do so few magmas have $\delta^{18}O$(WR) below 6‰ before 150 Ma? One could answer that examples are more common than is recognized and could be located by directed study. For instance, the low $\delta^{18}O$ samples from the Superior Province were found by targeting the stockwork feeder zone of a volcanogenic massive sulfide deposit and low $\delta^{18}O$ magmas are particularly abundant in volcanic areas undergoing glaciation such as Kamchatka where glacial melt-waters have very low $\delta^{18}O$ (Bindeman et al. 2004). In contrast, Balsley and Gregory (1998) propose that the genesis of low $\delta^{18}O$ magmas is a relatively rare event. While this may be correct, it does not address the increasing rarity for older terranes. Preservation must also be an important factor in the scarcity of old, low $\delta^{18}O$ igneous rocks. Hydrothermal alteration by surface waters is restricted to the relatively shallow crust, above the brittle-ductile transition. Such near-surface rocks are preferentially eroded. Thus, low $\delta^{18}O$ magmas have always been a feature on Earth, their volume has never been great, and they have been selected against in the rock record. There is no indication at present that the volume of such rocks has either increased or decreased systematically through time.

Constant $\delta^{18}O$ in the Archean Crust

The uniformity of $\delta^{18}O$ values throughout the Archean since 4.2 Ga is one of the most surprising and significant findings of this study. For approximately two billion years, the $\delta^{18}O$ of most igneous rocks averaged exactly the mantle value, a smaller number of rocks have 1–2‰ higher values, and no magmatic zircons are found with $\delta^{18}O > 7.5‰$. The data-rich histogram for 2.7 Ga Superior Province zircons (Fig. 7a) shows the same range of $\delta^{18}O$ as the smaller sample set for Barberton. The less-precise ion microprobe analyses of Early Archean zircons from the Jack Hills and the Beartooths are slightly higher on average, but within analytical uncertainty of these values.

Significant differences exist even within the relatively restricted and constant 2.5‰ range of Archean $\delta^{18}O$(Zrc). Values above 6‰ cannot be explained as pristine differentiates from mantle magmas. To be conservative, the lower limit of the non-mantle supracrustal field is set at 6.5‰ when poorer precision of ion microprobe data is discussed (vs. >6.0‰ for laser fluorination data). These higher $\delta^{18}O$ values indicate intracrustal recycling of surface materials into magma by melting or contamination. The ultimate source of higher values in the supracrustal materials was from low temperature interaction with water in the near-surface environment. Thus, the zircon record indicates that igneous rocks in the crust achieved small amounts of differentiation by ~4.3 Ga and oxygen isotope ratios maintained a steady state from ~4.2 to ~2.5 Ga.

Models for growth of the continental crust and rates of recycling via subduction vary greatly (Fig. 10b–e, see, Hurley and Rand 1969; Taylor and McLennan 1985; Armstrong 1981; 1991; Bowring and Housh 1995; Condie 1998; Kramers 2002; Bennett 2003; Campbell 2003). In ocean crust, the intensity of hydrothermal alteration may have been greater in the Archean, but the combined effects of high and low temperatures of exchange balanced each other such that no measurable shift in average $\delta^{18}O$ occurred (Muehlenbachs 1998). In continental crust, processes of crustal growth added magmas with near-mantle $\delta^{18}O$ values, while intracrustal recycling of supracrustal rocks created magmas with higher $\delta^{18}O$ (Simon and Lecuyer 2002).

It is remarkable that the steady state reflected by $\delta^{18}O$ of magmas corresponds to the main periods of crustal growth. This uniformity suggests that feedback mechanisms operated throughout the Archean. The creation of new continental crust is one consequence of thermal events that are accompanied by heating and remelting of existing crust (Kemp and Hawkesworth 2003). The oxygen isotope record shows that throughout the Archean, rates of crustal growth were balanced by rates of magmatic recycling in continental crust. In contrast, the trend towards higher $\delta^{18}O$ values, which begins at the end of the Archean, results from non-uniformitarian changes that altered the Archean steady state that had persisted for approximately two billion years. The rate of crustal growth declined and the effects of intra-crustal recycling increased.

Causes of secular change in the Proterozoic

The early Proterozoic was a time of great change on Earth with increased sedimentary environments following the period of crustal growth and cratonization in late Archean. Several important transitions occurred affecting: the composition and abundance of sedimentary and igneous rocks available for recycling; the rates of subduction; and differences in weathering as the atmosphere became more oxygen-rich and life flourished. These changes correlate in time to the major shift in $\delta^{18}O$(Zrc) and to trace element compositions (see Veizer and Mackenzie 2003; Kemp and Hawkesworth 2003; McLennan et al. 2005).

Sediments

Sediments are the dominant reservoir of high $\delta^{18}O$ material on Earth (Fig. 1). The quantity and $\delta^{18}O$ of sediments available for burial and recycling impacts the composition of resultant magmas. Thus, any process that changes the $\delta^{18}O$ of sediments, or changes the quantity of sediments available for melting, will have a corresponding effect on the $\delta^{18}O$ of igneous rocks and their zircons.

Figure 11 shows estimates for the evolving percentages of different sedimentary rock types through time (Veizer and Mackenzie 2003). Estimates are hypothetical before 3.0 Ga due to the incomplete rock record; later trends, based on more data, support the conclusion that Archean sediments were on average lower in $\delta^{18}O$. Archean sediments are dominated by greenstone-belt sequences, which are comprised largely of lower $\delta^{18}O$ volcaniclastic, pyroclastic, and sedimentary material of non-cratonic origin (Lowe 1994; Veizer and Mackenzie 2003). Continental and continental margin sequences were not common before 3.5 Ga and the Early Proterozoic marked a transition to major cratonic sedimentary sequences including an increase in high $\delta^{18}O$ clays and chemical sediments.

Shales comprise the largest high $\delta^{18}O$ sedimentary reservoir in the modern crust, but the fine-grained clastic sediments that are observed in the Archean are less ma-

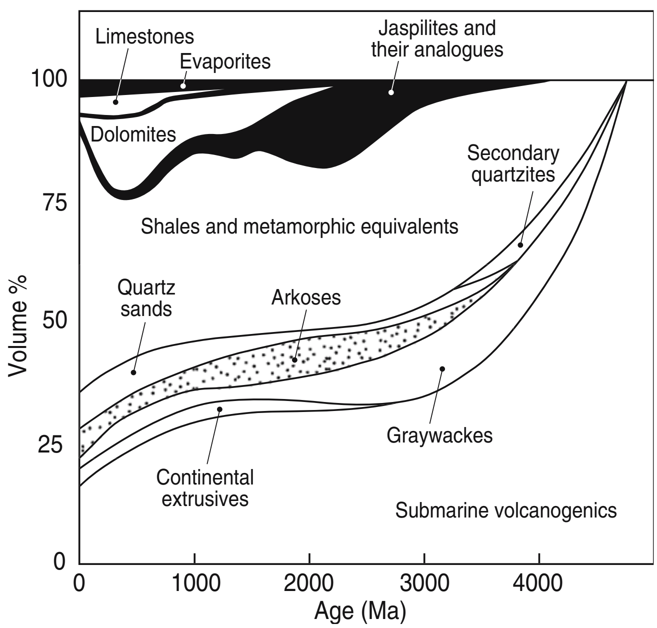

Fig. 11 Volume percent of different sedimentary rock types as a function of age. (from Veizer and Mackenzie 2003)

ture, richer in unaltered volcanic material, and lower in $\delta^{18}O$ (Longstaff and Schwarcz 1977; Shieh and Schwarcz 1978; Peck et al. 2000). Increasing maturity and clay content in clastic sediments have raised the bulk $\delta^{18}O$ through time. Furthermore, Veizer and Jansen (1985) present Sm-Nd model ages for sediments and conclude that the quantity of sediment increased through the Archean by erosion of relatively young igneous rocks within 250 million years of differentiation from the mantle. These "first cycle" rocks built up to nearly the present mass of sediment by ~2.5 Ga and recycling of sediments then became dominant (Windley 1995). Thus, while shales became quantitatively important after 3.5 Ga, the proportion of second generation shales with higher $\delta^{18}O$ increased after 2.5 Ga. Furthermore, in the Archean, aggressive weathering in CO_2-rich atmospheres may have stripped sediments of feldspar, leaving quartz-rich clastic rocks lacking in components that commonly make high $\delta^{18}O$ clays (Lowe and Tice 2004). Other changes in weathering pattern resulted from rising atmospheric oxygen levels at ca. 2.3 Ga that created more oxidized sediments and biological colonization of land. These changes facilitated weathering of primary feldspars and volcanic glass to form clays, which can be up to 30‰ higher in $\delta^{18}O$ than coexisting surface waters (Savin and Epstein 1970). Increased sedimentary reworking also contributed to increased marine deposits that were subsequently subducted. These long-term trends in weathering and clastic sedimentation contributed to the increase of magmatic $\delta^{18}O$ values during the Proterozoic. Thus, the early Proterozoic saw increased amounts of higher $\delta^{18}O$ sediments due to sedimentary recycling, and the growth of continents and epicontinental seas (Veizer 1983; Taylor and McLennan 1985; Eriksson 1995; Windley 1995; Condie et al. 2001).

Secular increases of 5–10‰ in the $\delta^{18}O$ of chemical sediments, limestones and cherts, are also reported during the Proterozoic that would further contribute to the change in magmas (Shields and Veizer 2002; Perry and Lefticariu 2003; Knauth and Lowe 2003; but see Land and Lynch 1996 for shales). The causes and significance of these trends are controversial. Competing interpretations propose a secular increase in $\delta^{18}O$ of the younger oceans; higher ocean temperatures in the Archean, or greater alteration of older sediments. The largest proposed changes in $\delta^{18}O$ of the ocean (> 10‰) are not consistent with the compositions of igneous rocks altered by seawater (Muehlenbachs 1998), but smaller differences might not be discerned. Likewise, the highest proposed ocean temperatures (≥70°C) must be reconciled with Precambrian continental glaciations, but smaller, localized, or intermittent increases in temperature could still lead to lower $\delta^{18}O$ sediments in earlier rocks and higher values in the Proterozoic. In addition to evolving $\delta^{18}O$ values, the quantities of high $\delta^{18}O$ carbonates and other chemical sediments are greater in the Proterozoic (Windley 1995; Veizer and Mackenzie 2003). Any combination of these processes would contribute to the secular change in magmas as seen in the zircon record.

Burial ± subduction

Burial is prerequisite for supracrustal rocks, whether sedimentary or volcanic, to be melted or assimilated by magma. For at least the past 2.5 Ga, subduction has been an important process to bury rocks and generate silicic and intermediate composition magmas, and some form of plate tectonics may have started much earlier (de Wit 1998). Nevertheless, other processes were operative in the Archean that do not require convergent tectonism (Bleeker 2002). Thick volcanic successions in extensional or plume-dominated environments can lead to burial and melting of sediments or igneous rocks. In a modern setting, caldera collapse and foundering of altered wall rocks caused magmatic $\delta^{18}O$ to shift by several permil at Yellowstone (Bindeman and Valley 2002). More extensive processes would have operated if Archean tectonics were plume- and rift-dominated. The earliest felsic crust may have formed on mafic basement in an "Iceland-like" environment (Kroner and Layer 1992) with mildly elevated $\delta^{18}O$ values seen as early as 4.3 Ga (Cavosie et al. 2005).

In contrast to plume tectonics, subduction reworks greater amounts of crust both by melting of subducted ocean crust with a sedimentary component from the continents and by subsequent melting within the continental crust caused by metasomatism and magmatic heating. Tectonic conditions were distinct in the Archean. Higher radiogenic heat production fostered vigorous greenstone-belt tectonics and many small unstable microplates. The average crust was younger and therefore hotter at the time of subduction. Crustal material was certainly returned to the mantle during the Archean, but as radiogenic heat-production declined, the style of subduction changed. In the Proterozoic, amounts of subducted sediment increased. Lowe (1992) has further proposed that Himalayan-style subduction first occurred in the late Proterozoic. If so, this process also could have contributed to the dominant high $\delta^{18}O$ magmatism first seen at 1.3 to 1.0 Ga in the Grenville Province. Thus, increased rate and changing style of subduction are both likely contributing causes of secular change of $\delta^{18}O$ in magmas.

The highest $\delta^{18}O$ values in Fig. 4 show a steady increase through the middle Proterozoic suggesting a gradual build-up in the amounts of ^{18}O-enriched magmas. Curiously, this trend has not been found to continue in the Phanerozoic. It may be significant that many of the highest $\delta^{18}O$ Proterozoic rocks were metamorphosed at depths of 20–30 km. Either Earth reached a new steady state with respect to oxygen isotopes at the end of the Precambrian or, more likely, the younger high $\delta^{18}O$ equivalents are not yet exhumed in great quantity from deep in the crust. This later scenario is demonstrated in the Sierra Nevada batholith; only a small proportion of 4–9 kb granites are exposed and they are systematically higher in $\delta^{18}O$ (Lackey et al. 2005a). Alternatively, it is possible that $\delta^{18}O$(Zrc) values above 10‰ are not common.

Thus, the secular rise of magmatic oxygen isotope ratios through the Proterozoic is explained by a combination of changes in the composition, availability, weathering, and burial of sediments that resulted from tectonic changes at the end of the Archean. The details of this important change will be elucidated as more geochemical systems and techniques are employed to study zircon and other retentive geochronology minerals.

Variation of $\delta^{18}O$ in the Mantle?

The dramatic trend to higher $\delta^{18}O$ in Proterozoic and Phanerozoic magmas and the accumulation of high $\delta^{18}O$ sediments and metasediments shows that the average $\delta^{18}O$ of continental crust has increased from 4.4 Ga to today. This increase must have been balanced by compensating changes in mass or $\delta^{18}O$ of other reservoirs. To identify these other reservoirs, a first order average $\delta^{18}O$ of continental crust can be estimated by consideration of sediments and magmas. Secondary processes of alteration and metamorphism are also important, but a more complete evaluation is beyond the scope of this paper and is not required for this discussion. The $\delta^{18}O$ of sediments range from 10 to over 40‰ and have been heavily studied. Veizer and Mackenzie (2003) review the evolution of sedimentary rocks and summarize studies concluding that 14% of the continental crust is composed of sediments with an average $\delta^{18}O$ of 17‰. The $\delta^{18}O$ of magmas can be estimated from Fig. 4 taking account of the age distribution (Fig. 10c), the average fractionation between zircon and whole rock (~1‰), and considering mafic magmas which are lower in $\delta^{18}O$ (Harmon and Hoefs 1995) and not fully represented by zircon-bearing samples. As previously discussed, low $\delta^{18}O$ magmas are not volumetrically significant. Taken together, the average continental crust is estimated to be 9–10‰. This represents an elevation of $\delta^{18}O$ of ca. 4‰ relative to the average mantle value of 5.5‰.

A 4‰ elevation in $\delta^{18}O$ for the entire continental crust would require a major reservoir for mass-balance. Only about 20% of this amount is compensated by low $\delta^{18}O$ of the oceans (0‰). This leaves the mantle as the remaining reservoir of sufficient size to compensate this change.

Mass-balance shows that if the entire 4‰ rise in average $\delta^{18}O$ of the continental crust was compensated by subduction of low $\delta^{18}O$ material into the upper 400 km of the mantle, the average decrease of $\delta^{18}O$ in the mantle over time would be approximately 0.1‰. The change in the mantle would be even less if subducted material is mixed more deeply. The possibility that the modern mantle is significantly heterogeneous in $\delta^{18}O$, due to failure of subducted material to mix on a sufficient scale, has not been supported by analysis of peridotites or oceanic basalts (Eiler 2001).

The best empirical evidence for $\delta^{18}O$ of zircon in equilibrium with the primitive mantle reservoir in the Archean comes from the Superior Province at 2.7 Ga. The average value for zircons from TTG's, volcanic rocks, and other non-sanukitoid magmas is 5.5‰. This value is 0.2‰ above the value estimated for modern magmas (Valley et al. 1998; Eiler 2001), suggesting either that terrestrial granitoids are slightly evolved relative to ocean basalts or that a secular change of 0.2‰ has occurred over the past 2.7 billion years. While this estimate is similar in magnitude and in the same direction as that predicted by mass-balance, the uncertainties are relatively large. The earlier Jack Hills zircons appear slightly heavier still, but better analytical precision by new generation ion microprobes will be necessary to evaluate this difference. Thus, while the secular change in $\delta^{18}O$ of the crust is significant and most reasonably balanced by subduction into the mantle, no detectable change in the average $\delta^{18}O$ of the mantle is either predicted or resolved by the present analysis. A similar conclusion was reached by Lowry et al. (2003) based on analysis of olivine in 3.8 Ga ultramafic rocks. The mass of the mantle is simply too large for its average $\delta^{18}O$ to be affected by the crust. More refined estimates are unlikely to change this conclusion.

Supercontinent cycles

It has long been recognized that radiogenic isotope ages are not uniformly distributed through time (Fig. 10b) and much discussion has centered on the question of whether magmatic differentiation and growth of continental crust is a reversible process. One view has held that once crust was created, it would never be returned to the mantle, and the age spikes (Fig. 10b) record the rate of crustal growth (Hurley and Rand 1969). In contrast, Armstrong (see Armstrong 1981, 1991; Sylvester 2000) argued for high rates of sediment subduction, that the growth rate of crust is underestimated by Hurley and Rand, and that growth of the crust to present mass was effectively complete by 3.5 Ga (Fig. 10c). The Armstrong model thus posits that there has been no net growth in the mass of continental crust through time and that new additions to the crust have been balanced by subduction in a steady state. Both Nd and Hf isotopic data support models of early differentiation of significant amounts of continental crust (Figs. 10d + e), however these isotope evolution diagrams do not resolve the question (Bennett 2003). The oxygen isotope data for Archean zircons provide a new constraint.

Recent models attribute the punctuated age distribution (Fig. 10b) to planet-scale cycles in the mantle, related to supercontinent or superplume events (Stein and Hoffman 1994; Condie 2000). Condie (2000) summarizes arguments that episodic periods of supercontinent formation in the Precambrian and probably in the Phanerozoic (Fig. 10) correlate to "catastrophic slab avalanching at the 660 km discontinuity". Whatever their causes, it is clear that these events have not altered the steady state recorded by $\delta^{18}O$ of zircons in the Archean. It is likely that the additional heat advected into the crust during magmatic pulses caused more melting and recycling of the crust, but maintained a constant proportion of primitive magma to remelted crust.

The changes in magmatic $\delta^{18}O$ starting at 2.5 Ga support the models of Taylor and McLennan (1985) and Kramers (2002) with high rates of growth for continental crust in the Archean and significantly slower growth after 2.5–1.9 Ga. The oxygen isotope record is more difficult to reconcile with the model of Armstrong (1981, 1991), which would produce higher $\delta^{18}O$ in Archean magmas, or with that of Hurley and Rand (1969) that suggests significant amounts of continental crust first appeared after 1.5 Ga. If crustal growth was rapid from 4.4 to ca. 1.9 Ga, the ratio of primitive mantle magma to supracrustal material was relatively high, diluting amounts of higher $\delta^{18}O$ magma and maintaining the subdued near-mantle $\delta^{18}O$ values seen for Archean zircons. After the major spikes of growth at 2.7 and 1.9 Ga, the proportions changed. Significantly larger amounts of continental crust were available to be altered and to form clastic and chemical sediments. At about the same time, the rates of mantle magmatism declined. Over the following one billion years, intracrustal recycling of these high $\delta^{18}O$ materials into magmas became increasingly more important and created the secular trend seen in Figs. 4 and 10a. It is also possible that the absence of still higher values ($>$ ca. 10‰) after 1 Ga represents establishment of a new steady state for oxygen isotopes in the continental crust, reflecting the mass of continental crust that was largely established by 1.9 Ga.

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Appendix 1

Oxygen isotope ratio, crystallization age, and location for magmatic zircons. Whole rock weight percentage SiO_2 is tabulated where available. References to previous work include published and unpublished sources. Table given as ESM, available at http://dx.doi.org/10.1007/s00410-005-0025-8

Appendix 2

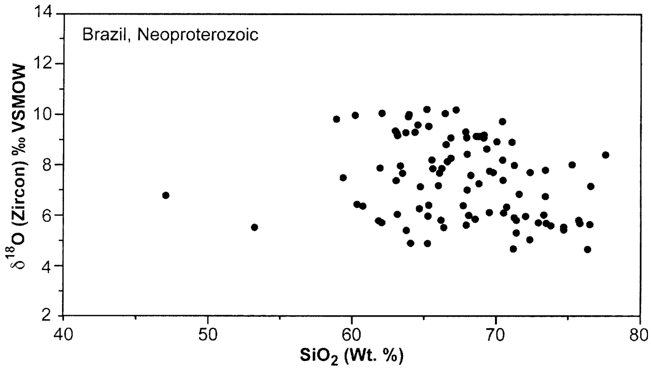

Fig. 12 Plot of $\delta^{18}O(Zrc)$ vs. SiO_2 content for magmatic zircons and their host rocks for 90 samples from the Neoproterozoic of Brazil

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