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# Proterozoic onset of crustal reworking and collisional tectonics: Reappraisal of the zircon oxygen isotope record

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## ABSTRACT

**A global U-Pb and  $\delta^{18}\text{O}$  zircon database shows temporal changes in the magmatic record related to changes in the degree of crustal reworking. The  $\delta^{18}\text{O}$  composition of bulk sediment remains relatively constant through geologic time, with a mean value of 14.9‰. In contrast, the  $\delta^{18}\text{O}$  values in magmatic zircons vary from relatively low values averaging ~6‰ in the Archean to increasingly higher and scattered values defining a series of peaks and troughs in post-Archean data. The degree of crustal reworking increases at times of supercontinent assembly. Therefore we attribute the pattern of post-Archean  $\delta^{18}\text{O}$  values recorded by magmatic zircons to a significant increase in the incorporation of high  $\delta^{18}\text{O}$  sediment in response to enhanced crustal thickening and reworking associated with the onset of collisional tectonics, especially during formation of supercontinents.**

## INTRODUCTION

Zircon is physically and chemically stable across a wide range of conditions. Its abundance in felsic and intermediate igneous rocks and refractory nature in sedimentary rocks make it a key mineral to understand the evolution of the continental crust (Hawkesworth and Kemp, 2006; Cawood et al., 2013). At the time of crystallization, oxygen isotopes in zircon reflect the  $\delta^{18}\text{O}$  values of the host magma and therefore the relative contributions of material from the mantle and continental crust, with  $\delta^{18}\text{O}$  values between 4.7‰ and 6.0‰ taken as indicative of the former (Valley et al., 1998; Page et al., 2007; Grimes et al., 2011). Excluding zircons damaged by radiation or thermal dilation (e.g., Cherniak and Watson, 2001; Booth et al., 2005), any significant increase from those mantle values is interpreted as incorporation of supracrustal material (Valley et al., 2005) and results in melts with elevated zircon  $\delta^{18}\text{O}$  values (e.g., Valley et al., 1994; Roberts et al., 2013).

To investigate changes in the degree of crustal reworking in continental magmas through time, we compiled a global database of oxygen isotope analyses of zircon (Table DR1 in the GSA Data Repository<sup>1</sup>). Previous such studies indicate that Earth's Archean crust was dominated by mantle-like oxygen isotopic values, whereas

post-Archean zircons have a greater range in  $\delta^{18}\text{O}$  (Valley et al., 2005; Dhuime et al., 2012). It has remained unresolved whether the former signifies minimal crustal reworking or a restricted range of  $\delta^{18}\text{O}$  (based on whole-rock analysis) in Archean sedimentary rocks, and whether the latter reflects increased contribution from upper crustal melts and/or an increasingly evolved supracrustal reservoir available for reworking. Furthermore, it has variably been proposed that the envelope of maximum  $\delta^{18}\text{O}$  values in magmatic zircons increases from the Paleoproterozoic to the present (Valley et al., 2005), or that  $\delta^{18}\text{O}$  in zircon increased until ca. 1.1 Ga and decreased until the present (Van Kranendonk and Kirkland, 2013).

We reevaluate the extent to which the  $\delta^{18}\text{O}$  values of sedimentary rocks have changed through time and compare the  $\delta^{18}\text{O}$  values of zircon with that of the sedimentary record. The zircon  $\delta^{18}\text{O}$  database presented in Table DR1 highlights an increase in elevated  $\delta^{18}\text{O}$  material above an essentially constant Hadean–Archean background between ca. 2.5 and 2.15 Ga. This is attributed to the incorporation of low-temperature fractionated supracrustal material during the earliest Proterozoic that we interpret as linked to the onset of significant crustal thickening and continental collisions (e.g., Ernst, 2009; Dhuime et al., 2012; Keller and Schoene, 2012).

## METHODS

Our database combines ~6300  $\delta^{18}\text{O}$  analyses of detrital and igneous zircon grains (Figs. 1A and 1B; Table DR1). We exclude data reported from metamorphic grains or overgrowths (which tend to be extremely fractionated; e.g., Bowman et al., 2011) as well as from zircons with U-Pb ages >10% discordant. The U-Pb age distribution of the data compiled in this study

is similar to that for the modern river zircon database (Campbell and Allen, 2008) and the database of Voice et al. (2011) of ~200,000 zircon U-Pb ages. This affirms that our database broadly represents the exposed crustal record, although the extent to which tectonic processes may bias that record remains a subject of debate (Hawkesworth et al., 2010; Condie et al., 2011; Cawood et al., 2013).

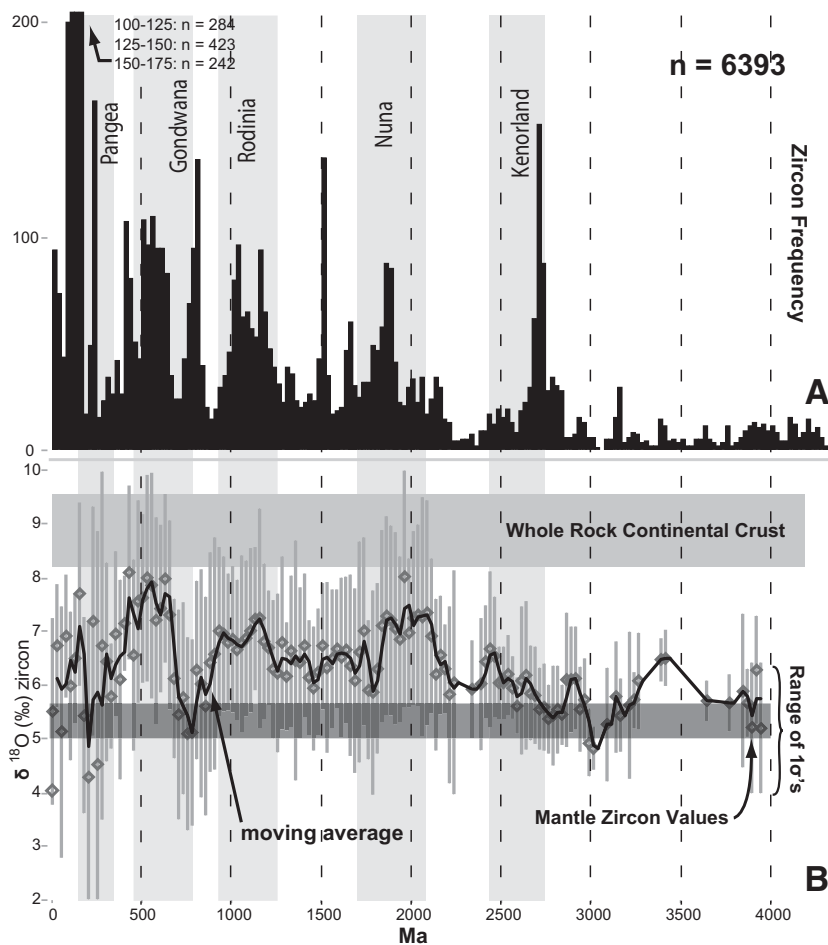
Our database differs from that used previously by Valley et al. (2005) in that it incorporates nearly three times the number of analyses and demonstrates (1) a broader range (though statistically equivalent mean) of Archean  $\delta^{18}\text{O}$  values, +2.4‰ to +8.8‰ (average = 5.9‰  $\pm$  0.9‰, 1 $\sigma$ ) versus +2.4‰ to +7.5‰ (average = 5.8‰  $\pm$  0.7‰, 1 $\sigma$ ); (2) unimodal distribution of Proterozoic  $\delta^{18}\text{O}$  values (Fig. 2; note the similarity with Phanerozoic values) with low skewness ( $\sigma = 1.0$ ); and (3) 5% of analyses are above the composition-time envelope of  $\delta^{18}\text{O}$  values previously proposed (Valley et al., 2005). We parse and analyze the updated database using a bin-size optimization procedure (Shimazaki and Shinomoto, 2007) to avoid pitfalls associated with bin widths that are unjustifiably small relative to analytical errors (as in Voice et al., 2011), or are so large as to limit interpretive resolution (as in Dhuime et al., 2012).

We have used the natural subdivisions of zircon age frequency within the compiled data set (Fig. 1A) as the basis for evaluating temporal isotopic shifts and to divide the  $\delta^{18}\text{O}$  data set into the following time intervals: pre–3100 Ma, 3100–2450 Ma, 2450–2000 Ma, 2000–1600 Ma, 1600–1300 Ma, 1300–900 Ma, and 900–400 Ma (Fig. 2A). We note that values of  $\delta^{18}\text{O}$  from zircons with ages younger than 400 Ma are lower than those immediately preceding them (Fig. 1B). This is likely due to the disproportionate sampling of atypical compositions and/or petrotectonic associations for the post–400 Ma data, e.g., the extremely low  $\delta^{18}\text{O}$  magmas from the Isle of Skye (Gilliam and Valley, 1997; Monani and Valley, 2001) and Yellowstone (Bindeman and Valley, 2001; Bindeman, 2008). Given these uncertainties and the smaller data set within this timeframe, we do not consider it further in this study.

Zircons from different time periods exhibit different distributions of  $\delta^{18}\text{O}$  (Fig. 2B) that can be grouped into two categories (Fig. 2B): type 1, characterized by a narrow peak between

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<sup>1</sup>GSA Data Repository item 2014158, Table DR1 ( $\delta^{18}\text{O}$  values in zircon), and Table DR2 (sedimentary proportions model and average  $\delta^{18}\text{O}$  compositions of the sedimentary rock types), is available online at [www.geosociety.org/pubs/ft2014.htm](http://www.geosociety.org/pubs/ft2014.htm), or on request from [editing@geosociety.org](mailto:editing@geosociety.org) or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.



**Figure 1. A: Histogram of compiled U-Pb ages with accompanying  $\delta^{18}\text{O}$  values overlain on age ranges of supercontinents (see Campbell and Allen, 2008; Bradley, 2011). B: Distilled compilation of ~3300  $\delta^{18}\text{O}$  analyses of zircon versus U-Pb age plotted as means and standard deviations for 25 m.y. bins. Also plotted are range of average mantle and continental crust values (Valley et al., 1998) and moving average of  $\delta^{18}\text{O}$  bins.**

5.5‰ and 6.5‰ with low variance and skewed toward enriched isotopic values (time intervals 3100–2450, 2450–2000, and 1600–1300 Ma); and type 2, marked by a broad peak between 6.5‰ and 8.0‰ with high variance and near-normal distribution (time intervals 2000–1600, 1300–900, and 900–400 Ma).

The secular change in  $\delta^{18}\text{O}$  of zircons from relatively low and constant during the Archean to a systematic increase through the Proterozoic Era and Phanerozoic Eon was explained by Valley et al. (2005) to reflect a shift in the  $\delta^{18}\text{O}$  composition of shale through time (see also Land and Lynch, 1996) in addition to an enhanced rate of subduction at the end of the Archean. However, pelitic rocks form only ~40% of the bulk sediment budget post-3.5 Ga. We have therefore used the relative abundance of different sedimentary rock types and their representative whole-rock  $\delta^{18}\text{O}$  compositions (see Eiler, 2001; Valley et al., 2005; Bindeman, 2008) to assess the  $\delta^{18}\text{O}$  composition of global bulk sediment through time. We adopt the proportions of sedimentary rocks determined by

Ronov (1964), using a smoothed estimate of present-day distributions preserved within continental interiors (Fig. 3; see also Table DR2). The total preserved mass of sedimentary rock prior to 3 Ga is small, which hinders estimating their proportions; nonetheless, the Ronov (1964) treatment is considered appropriate for broad-scale hypothesis testing. We contrast the proportions proposed by Ronov (1964) with those proposed by K. Condie (2014, personal commun.; see Fig. 3).

Shales, cherts, and carbonate rocks appear to have shifted toward higher  $\delta^{18}\text{O}$  values from the Archean to the present by 3‰–5‰ (Land and Lynch, 1996; Shields and Veizer, 2002; Perry and Lefticariu, 2003; Knauth, 2005), whereas sandstones and submarine volcanogenic rocks have remained nearly constant (Kolodny and Epstein, 1976; Anderson and Arthur, 1983; Eiler, 2001). Assuming that the relative proportions of these lithologies are representative of global sedimentary rock volumes through time, their integrated isotopic composition can be estimated. Although Figure 3 does not illustrate

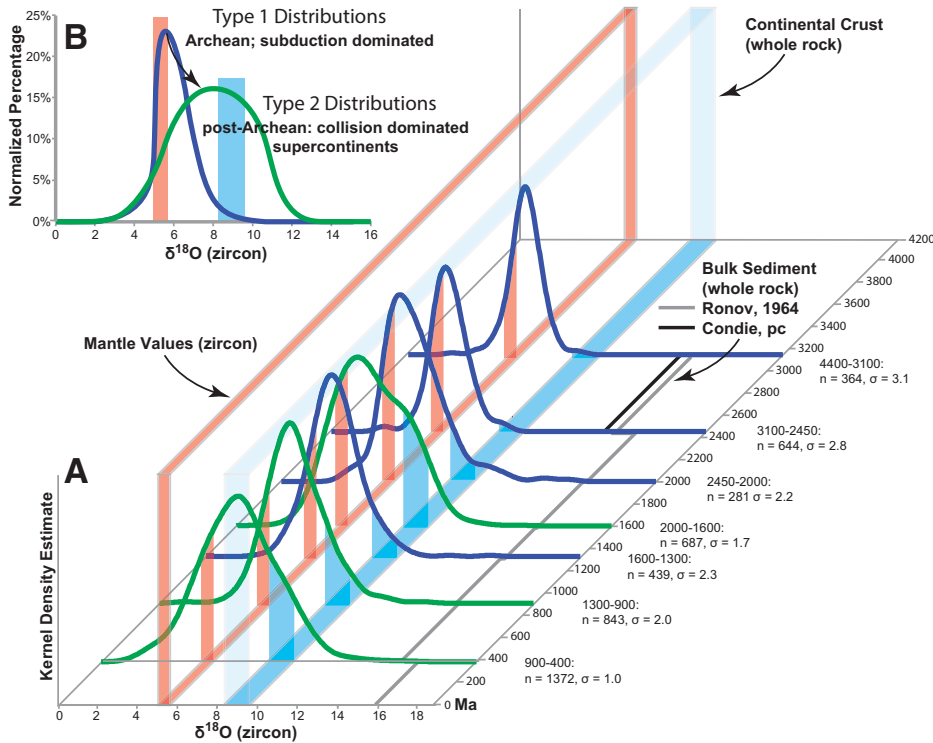
the preservation bias of large sedimentary packages (Bradley, 2008), it highlights overall temporal trends (Veizer and Mackenzie, 2003) and reveals a relatively constant average of  $14.9\text{‰} \pm 1.0\text{‰}$  ( $2\sigma$ )  $\delta^{18}\text{O}$  for bulk continental sediment from the Archean through Phanerozoic. This implies that the extent of fractionation of  $^{18}\text{O}$  within the sedimentary environment has not changed significantly since the Archean.

We evaluate temporal changes in supracrustal input at a resolution that divides the data set into 25 m.y. bins (bin width optimization parameters of Shimazaki and Shinomoto, 2007, suggest 23.1 m.y.). We then use the average  $\delta^{18}\text{O}$  bulk sediment (14.9‰, discussed herein) and mantle (whole rock) values (5.5‰; Bindeman, 2008) as end members of a mixing trend to parameterize what is termed the “reworking index” (Fig. 4). Our results show a subdued moving average with relatively minor variation in crustal reworking from ca. 4.0 to 2.5 Ga, but a marked increase in reworking after 2.5 Ga accompanied by a pulsed pattern of sequential increases bounded by abrupt decreases at 1800 Ma, 850 Ma, and 350 Ma (Fig. 4).

## DISCUSSION

The patterns of peaks and troughs in zircon  $\delta^{18}\text{O}$  values (Fig. 4) broadly coincide with zircon age distribution profiles, excluding the ca. 2.7 Ga U-Pb age peak, which has subdued  $\delta^{18}\text{O}$  values (Fig. 1A). Pre-2.5 Ga zircons define type 1  $\delta^{18}\text{O}$  distributions (Fig. 2B), with means near to mantle values and limited crustal reworking. Type 2 distributions (Fig. 2B), in contrast, have means at higher  $\delta^{18}\text{O}$  values and indicate that the post-2.5 Ga peaks in zircon age frequency are correlative to greater crustal reworking and harbingers of supercontinent tectonics. This is likely an outcome of continental collision and times of increased preservation of continental crust. After the initial formation of substantial crustal blocks, the geodynamics of plate convergence through time increasingly involved continental collisions accompanied by significant crustal reworking, leading to isotope ratios that deviate from depleted mantle compositions (see also Hawkesworth et al., 2010; Cawood et al., 2013). These findings cast doubt on the hypothesis that zircon age frequency is associated with increased juvenile crustal generation during mantle overturn or plume events (Stein and Hofmann, 1994; Rino et al., 2004; Stein and Ben-Avraham, 2007; Arndt and Davaille, 2013).

The onset of modern plate tectonics is thought to have begun by the Neoproterozoic (Cawood et al., 2006; Ernst, 2009; Condie and Kröner, 2013; Dhuime et al., 2012). The earliest subduction zones were likely dominated by the formation and accretion of oceanic arcs accompanied by minimal crustal reworking and significant recycling into the mantle (Condie and Kröner, 2013). Over time con-



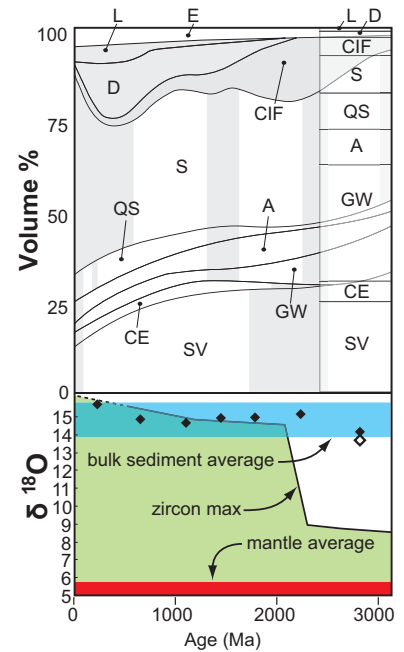
**Figure 2. A:** Distributions of  $\delta^{18}\text{O}$  analyses of zircons normalized to total analyses within specific temporal subdivisions (see text) superimposed on mantle values of Valley et al. (1998). To test sensitivity of our chosen bin widths, boundaries were adjusted  $\pm 50$  m.y.; this had negligible effect on  $\delta^{18}\text{O}$  distributions due to small number of analyses near window margins relative to thickness of our chosen windows. Calculation of  $\delta^{18}\text{O}$  composition of bulk sediment based on sedimentary models of Ronov (1964) and K. Condie (2014, personal commun.) is discussed in text. **B:** Schematic diagram of  $\delta^{18}\text{O}$  distributions of subduction- and collision-dominated temporal subdivisions.

tinued subduction processes led to increased volume and thickness of preserved continental crust and sedimentary differentiation (Ernst, 2009). These developments in Earth's thermo-mechanical attributes were accompanied by continental collisions, crustal thickening, and an increase in the degree of crustal reworking post-2.5 Ga. The link between increases in the crustal reworking index and the development of supercontinents highlights the role of continental collision in the preferential preservation of peaks of U-Pb crystallization ages in the continental crust (Fig. 1). These conclusions are consistent with other isotopic proxies (Zn in banded iron formation, Pons et al., 2013; Sr in seawater, Shields and Veizer, 2002) that are linked to the appearance of large, subaerially exposed continental masses near the Archean-Proterozoic boundary.

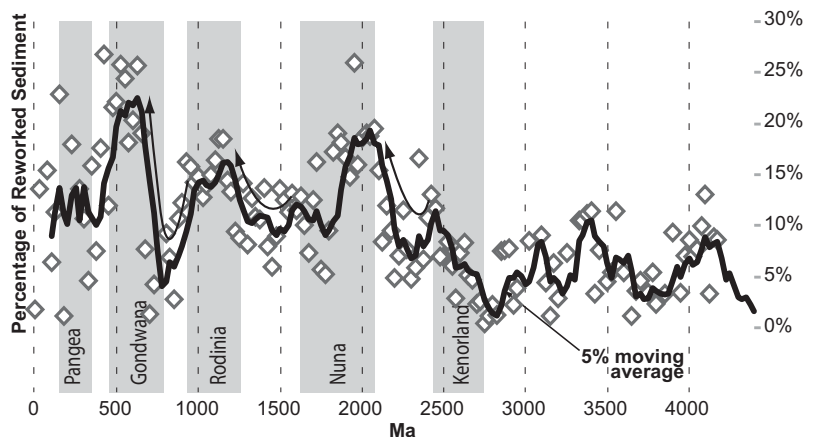
The great oxygenation event would have promoted enhanced influx of highly fractionated  $\delta^{18}\text{O}$  sedimentary material to basins, material that, when reworked via tectonomagmatic processes, could have contributed to the dramatic increase in zircon  $\delta^{18}\text{O}$  between 2.5 and 2.15 Ga (Campbell and Allen, 2008). Interpretations of secular evolutions within this critical age window will benefit especially from future coupled U-Pb and  $\delta^{18}\text{O}$  analyses in situ in zircons.

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**Figure 3. Upper panel:** Volume percent of different sedimentary rock types as function of age (from Ronov, 1964). Sedimentary proportions during Archean proposed by K. Condie (2014, personal commun.) are also displayed. Shaded areas are lithologies and time intervals wherein  $\delta^{18}\text{O}$  compositions are constrained (Table DR1; see the Data Repository [see footnote 1] for details and references). SV—submarine volcanogenics, CE—continental extrusives, GW—graywacke, A—arkose; QS—quartz sands, S—shale, CIF—cherts and/or iron formations, D—dolomite, L—limestone, E—evaporites. **Lower panel:**  $\delta^{18}\text{O}$  (whole rock) values of bulk sediment using temporal subdivisions described in text superimposed over envelope of maximum zircon  $\delta^{18}\text{O}$  values within compiled database. Average mantle  $\delta^{18}\text{O}$ : 5.5‰–5.9‰ (Bindeman, 2008). Open diamond is average Archean bulk sediment composition using sedimentary proportions proposed by K. Condie (2014, personal commun.).



**Figure 4. Reworking index** plotted through time, calculated by plotting average  $\delta^{18}\text{O}$  composition of zircons (in 25 m.y. bins) along univariant mixing line between  $\delta^{18}\text{O}$  composition of mantle (5.5‰) and calculated average bulk sediment ( $14.9\text{‰} \pm 1.0\text{‰}$ ,  $2\sigma$ ). Note that zircons with low  $\delta^{18}\text{O}$  values ( $< 5.0\text{‰}$ ) are probably due to hydrothermal alteration (Valley et al., 2003).

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