Oxygen isotope perspective on crustal evolution on early Earth: A record of Precambrian shales with emphasis on Paleoproterozoic glaciations and Great Oxygenation Event

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Abstract

We present stable isotope and chemical data for 206 Precambrian bulk shale and tillite samples that were collected mostly from drillholes on all continents and span the age range from 0.5 to 3.5 Ga with a dense coverage for 2.5-2.2 Ga time interval when Earth experienced four Snowball Earth glaciations and the irreversible rise in atmospheric O₂. We observe significant, downward shift of several ‰ and a smaller range of δ¹⁸O values (7 to 9‰) in shales that are associated with the Paleoproterozoic and, potentially, Neoproterozoic glaciations. The Paleoproterozoic samples consist of more than 50% mica minerals and have equal or higher chemical index of alteration than overlying and underlying formations and thus underwent equal or greater degrees of chemical weathering. Their pervasively low δ¹⁸O and δD (down to -85‰) values provide strong evidence of alteration and diagenesis in contact with ultra-low δ¹⁸O glacial meltwaters in lacustrine, deltaic or periglacial lake (sikussak-type) environments associated with the Paleoproterozoic glaciations. The δD_{silicate} values for the rest of Precambrian shales range from -75 to -50‰ and are comparable to those for Phanerozoic and Archean

shales. Likewise, these samples have similar ranges in $\delta^{13}\text{C}_{\text{org}}$ values (-23 to -33‰ PDB) and C_{org} content (0.0 to 10 wt.%) to Phanerozoic shales.

Precambrian shales have a large range of $\delta^{18}\text{O}$ values comparable to that of the Phanerozoic shales in each age group and formation, suggesting similar variability in the provenance and intensity of chemical weathering, except for the earliest 3.3-3.5 Ga Archean shales, which have consistently lower $\delta^{18}\text{O}$ values. Moreover, Paleoproterozoic shales that bracket in age the Great Oxidation Event (GOE) overlap in $\delta^{18}\text{O}$ values. Absence of a step-wise increase in $\delta^{18}\text{O}$ and δD values suggests that despite the first-order change in the composition of the atmosphere, weathering cycle was not dramatically affected by the GOE at ~2.4-2.3 Ga. Shales do not show comparable $\delta^{18}\text{O}$ rise in the early Phanerozoic as is observed in the coeval $\delta^{18}\text{O}$ trends for cherts and carbonates. There is however a sharp increase in the average $\delta^{18}\text{O}$ value from the Early Archean to the Late Archean followed by a progressively decelerating increase into the Phanerozoic. This decelerating increase with time likely reflects declining contribution of mantle-extracted, normal- $\delta^{18}\text{O}$ crust and lends support to crustal maturation and increasing ^{18}O sequestration into the crust and recycling of high- $\delta^{18}\text{O}$ sedimentary rocks. This secular increase in the $\delta^{18}\text{O}$ composition of the continental crust could have also had a mild effect on seawater $\delta^{18}\text{O}$ composition.

1. INTRODUCTION

Stable (C, S, N, H, and O) isotopes in sedimentary rocks and surficial materials have been widely used over the last six decades to constrain interaction between life and environment, changes in the atmosphere and ocean, evolution of life, climate changes, and secular trends in seawater composition. Shales and mudstones constitute 50 to 80% of total sedimentary rock mass (Pettijohn, 1957; Ronov and Yaroshevsky, 1969). Their bulk chemical and isotopic composition is thought to reflect the average chemical and isotopic composition of the exposed continental crust (Goldschmidt, 1933) and elemental and isotopic fluxes related to weathering. Mineralogically, shales are made of a mixture of two principle components: 60-

70% of clays (kaolinite, chlorite, illite, and smectite) and 20-30% of quartz, with other authigenic and detrital minerals being minor constituents. The proportion of these minerals in shales does not change with time (Shaw and Weaver, 1965). While carbonates and cherts have been utilized extensively to isotopically characterize the evolving hydrosphere, similar isotopic studies of shales have lagged behind. Specifically, the effect of the transition from the anoxic to oxygenated atmosphere (the Great Oxygenation Event; GOE) and Paleoproterozoic ice ages on the oxygen isotope composition of Precambrian shales has not been explored.

1.1 Oxygen isotopes of mudstones and their constituent minerals: what do they reflect?

Oxygen isotopes may provide a proxy for the relative role of physical vs. chemical (including biological) weathering because oxygen is a major constituent of crystal lattices of source rocks (igneous, sedimentary, and metamorphic) and secondary (authigenic) minerals, allowing quantification of intensity of chemical weathering under different climatic conditions. The results of previous studies (Savin and Epstein, 1970a, b; Yeh and Savin, 1976; Yeh and Epstein, 1978; Churchman et al., 1976; Savin and Lee, 1988; Sheppard and Gilg, 1996) demonstrate that:

1) clays and quartz components in shales are isotopically heavy, shifted up by 16 to 25‰ with respect to mantle values, but were not in isotopic equilibrium with ambient waters during weathering, which implies that oxygen from the source rock crystal lattices was incorporated into newly formed clay minerals;

2) rates of oxygen isotope exchange of these clays (once they are formed) with seawater are exceedingly slow and thus shales undergo little isotope exchange with seawater after being deposited into marine basins; diagenesis retains the $\delta^{18}\text{O}$ values within 1 to 2‰ of original values (Savin and Epstein, 1970b; Yeh, 1980);

3) diagenetic reactions occur within narrow temperature window of 80 to 120°C (Eberl, 1993; Clauer et al. 1990). The $\delta^{18}\text{O}$ values for shales deposited in marine vs. lacustrine

environments differ by no more than 1.4‰ (Land and Lynch, 1996), implying limited exchange with seawater and meteoric porewaters upon deposition;

4) hydrogen isotopes on the other hand are easily altered with depth and homogenized during interaction with porewaters, diagenesis, and lithification (Yeh, 1980). Savin and Epstein (1976) however argued that due to low shale porosity, bulk shale D/H ratios record exchange during diagenesis, but plot with scattered, yet meaningful offset, on the $\delta^{18}\text{O}$ vs. δD diagram;

5) lithification and occlusion of pore spaces in clastic sediments often takes $\sim 10^5$ - 10^6 years (Pettijohn, 1957) and involves solution-reprecipitation in contact with pore fluids. After diagenesis mudstone porosity changes from 30 to <5%, making shales virtually impermeable to subsequent alteration;

6) due to primary small grain-size and low final, post-diagenetic permeability of shales, Darcy's percolation of isotopically and chemically distinct post-diagenetic waters is limited upon completion of diagenesis and expulsion of porewaters. It is thus thought that O and even H isotopic values of shales are preserved without significant change unlike those in other sedimentary lithologies such as carbonates, cherts, and sandstones (Savin and Epstein, 1976; Land and Lynch, 1996). It takes rather extreme temperatures or volumes of fluids to impart changes onto lithified shales that also results in petrographically-recognizable recrystallization into coarser-grained materials (Sheppard and Gilg, 1996), often accompanied by development of schistosity.

We illustrate the effect of weathering on $\delta^{18}\text{O}$ values of secondary quartz and mica on **Fig. 1**. With an increase in the temperature of weathering from +1°C to +28°C isotope fractionations decrease by 5 to 10‰ for chlorite, kaolinite, illite, smectite, and secondary quartz, and by 6.5‰ for an average shale consisting of 67% clay and 33% quartz. This should result in lower $\delta^{18}\text{O}$ values of weathering products at higher T provided that isotopic equilibrium was approached. However, meteoric waters in tropical regions also have higher $\delta^{18}\text{O}$ and δD values, because they are closer to the marine source and due to lower water-vapor isotope fractionation at higher temperatures, resulting in the difference between the tropical and mid-latitude meteoric waters

of 7 to 12‰ (e.g., Dansgaard, 1964; Jouzel et al. 1994; West et al., 2010). Combined these effects result in increasing oxygen isotope values of weathering products with T (**Fig. 1**), but once ~18-22°C is reached, $\delta^{18}\text{O}$ values of authigenic quartz and clay stay the same regardless of T (and latitude of weathering). This observation might explain similar $\delta^{18}\text{O}$ values of wind-blown authigenic quartz silt and loess from different areas that tend to cluster around $+19 \pm 2\text{‰}$ (Churchman et al., 1976). It thus seems reasonable to assume that $\delta^{18}\text{O}$ values of bulk shales would predominantly reflect weathering setting: primarily $\delta^{18}\text{O}$ values of meteoric water and surface temperature, both of which depend on paleolatitude and climate. Mudrocks also have detrital component with lower $\delta^{18}\text{O}$ values, with its contribution decreasing, scaled to intensity of chemical weathering, when surface temperature increases. The effects of mixing of detrital and authigenic components are shown by the dashed line on Fig. 1, and this curve maintain concave up shape. We will return to these topics in the Discussion.

1.2 Motivation for this work

Almost 45 years have gone since the last large-scale investigation of oxygen and hydrogen isotope values of shales and sediments by the Caltech Group and other researchers (Savin and Epstein, 1970a, b; Lawrence and Taylor, 1971; Longstaffe and Schwartz, 1977). We now have better geochronological constraints and fresh drillcore samples that cover the Precambrian, deeper understanding of the events and climate changes that occurred during that time, and more precise analytical methods that utilize smaller amounts of material.

While several recent studies have analyzed Phanerozoic shales and clays (Stern et al., 1997; Rosenau and Tabor, 2013; Mix and Chamberlain, 2014), almost no data was published on Precambrian shales, and those that were earlier published suffered from poor age constraints and small datasets (e.g., Viswanathan, 1974; Longstaffe and Schwartz, 1977). This study helps to fill this knowledge gap by providing new data for $\delta^{18}\text{O}$, δD , $[\text{C}_{\text{org}}]$, and $\delta^{13}\text{C}_{\text{org}}$ values for 3.5-0.5 Ga shales (**Table A1, 2**) with a particular emphasis on the 2.5-2.2 Ga time interval, when the Earth experienced the transition to the oxygenated atmosphere, Snowball glaciations, and

major perturbations in the biogeochemical carbon cycle. We also test whether the GOE at ~2.4-2.3 Ga caused a stepwise change in a continental weathering style. Specifically, do shales record a step-function change in $\delta^{18}\text{O}$ values and D/H ratios as do $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values of sedimentary sulfates and sulfides (Farquhar and Wing, 2005)? Did the rise of atmospheric oxygen, oscillations in pCO_2 , decrease in atmospheric CH_4 concentrations, and emergence of aerobic microbial life on land affect continental chemical weathering rates and accompanying isotopic fractionations? Are Snowball Earth glaciations reflected in shale oxygen isotope record? Furthermore, what are isotopic effects of sedimentary sequestration, continental crust growth, four supercontinent cycles and gradual increase in continental freeboard during the investigated time interval starting at 3.5 Ga? Finally, what imprint (if any) did $\delta^{18}\text{O}$ values of seawater leave on these lithologies during diagenesis?

2. SAMPLES AND ANALYTICAL METHODS

2.1 Samples

Samples analyzed in this work (**Table A1**, Supplementary Material) were selected primarily from drillcores. Having fresh samples from drillcores uncompromised by recent weathering is a must for this kind of investigation especially for tropical regions such as Africa and Australia. The degree of metamorphism of the studied formations is not higher than lower greenschist facies. Absolute ages for these formations and their stratigraphic position with respect to four Paleoproterozoic glaciations are summarized in **Table A1**, based on previous and ongoing geochronologic studies. We also utilized data from the literature for Phanerozoic shales (Land and Lynch, 1996) and compiled previously published data for Precambrian shales and metasediments (Viswanathan, 1974; Longstaffe and Schwartz, 1977; Huebner et al. 1986).

2.2 Analytical Methods

Detailed description of the analytical methods is given in the supplementary material with a short summary provided below. We obtained oxygen and hydrogen isotope data for bulk shale

samples by laser fluorination and continuous flow TC-EA methods, respectively, integrated with MAT-253 mass spectrometer (e.g., Bindeman, 2008 and Bindeman et al. 2012). δD data are reported relative to NBS30 biotite value (-65,7‰) for comparison purposes with previously run shales. For analysis of C and O isotope values of carbonate in carbonate-bearing samples we used standard procedure of 2h phosphoric acid digestion at 70°C on GasBench II attached to the same MAT-253 mass spectrometer in a continuous flow mode. Concentrations of total organic and inorganic carbon and sulfur were determined on an Eltra IR C/S analyzer. Analyses of $\delta^{13}C_{org}$ values were performed using a CostechTM 4010 EA coupled to a Delta V plus mass spectrometer via ConFlo III and normalization procedures followed those in Coplen et al. (2006). Major and trace element concentrations of 55 bulk shales were determined by XRF using Li-B fused discs and Rigaku instrument. Quantitative mineralogy for selected shale samples was determined with XRD by scanning for ~1 h at 70° 2 ϕ angle.

3. RESULTS

3.1 Mineralogical and chemical composition of investigated shales

Bulk shale analysis that we employ despite its drawbacks related to mixing of moderately different proportions of clays (mica) vs. quartz has advantage of being immune to intra- and inter-mineral redistribution of O isotopes as a result of largely unconstrained diagenetic and lower-grade metamorphic histories of individual samples. Bulk shale, in this approach, provides a good proxy at the common level of comparison for shales across latitudes as explained in **Fig. 1**, regardless of the degree of closed-system metamorphism. Data on quantitative bulk vs. mica $\delta^{18}O$ measurements for Phanerozoic shales from Land and Lynch (1996) lend further support to using bulk shale samples as they are typically enriched only by ~1‰ with respect to mica (**Fig. 2a**).

Using XRD analysis, we obtained proportions of minerals for a subset of 18 investigated shales that have a large range of SiO₂ and $\delta^{18}O$ values (**Table A3**) in order to check if there is positive correlation of $\delta^{18}O$ values with modal% of quartz and SiO₂ content of rocks since

authigenic quartz has higher than mica $\delta^{18}\text{O}$ values; see **Fig. 1**. Instead, we found lack of correlation among these parameters (**Fig. 2b**), indicating that the use of bulk shales vs. their clay or quartz components, does not significantly bias our results. Major element composition of studied shales (**Table A4**) was used to calculate Chemical Index of alteration (CIA). The CIA (cf. Nesbitt and Young, 1982) measures intensity of chemical weathering including alteration of feldspars into clays: $\text{CIA} = \text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO}) * 100$, where Al_2O_3 , Na_2O , K_2O , and CaO are molecular quantities of silicate fraction of a rock (CaO in carbonates and phosphates is not included). For feldspars CIA is 50, while for clays and mudstone formed under extreme weathering conditions this parameter approaches 100. The CIA is listed in **Table A1**.

3.2 The $\delta^{18}\text{O}$ values of shales through time

Histograms in **Fig. 3** and $\delta^{18}\text{O}$ values vs. age plot on **Fig. 4** show new and compiled literature data for $\delta^{18}\text{O}$ values in shales arranged into age groups. With the exception of shales deposited in association with the Huronian and Neoproterozoic Ice Ages as discussed below, there is an overall increase in $\delta^{18}\text{O}$ values from the Early Archean to the present with the average values (± 1 stdev): $9.31 \pm 0.36\text{‰}$ (3.5-3.4 Ga), $9.7 \pm 2.4\text{‰}$ (3.2-3.0 Ga), $12.7 \pm 3.0\text{‰}$ (2.7-2.5 Ga); $14.1 \pm 2.4\text{‰}$ (2.15-1.8 Ga), $16.0 \pm 2.0\text{‰}$ (1.47-1.35 Ga), $14.7 \pm 2.7\text{‰}$ (1.13-0.95 Ga), $18.8 \pm 2.2\text{‰}$ (0.85-0.75 Ga), $15.7 \pm 2.3\text{‰}$ (0.5-0.25 Ga), $16.2 \pm 2.5\text{‰}$ (0.25-0 Ga) and $+19.0\text{‰}$ for the modern shale from Savin and Epstein (1970b). However, the range of $\delta^{18}\text{O}$ variations, the parameter that encompasses a variety of surface weathering conditions and $\delta^{18}\text{O}$ values of ambient waters, stays approximately the same (8 to 20‰), with the exception of the oldest, 3.4-3.0 Ga shales, which have a lower and narrower 8 to 13‰ range. The oldest shales in our dataset include those from the Barberton greenstone belt, one sample from the Superior craton from Longstaffe and Schwartz (1977), and ~ 3.5 Ga Limpopo metapelites (Huebner et al., 1986). When plotted vs. age, there is a gradual increase in $\delta^{18}\text{O}$ values with decreasing age (**Figs. 4, 8**). There is sharp increase of $\sim 2.4\text{‰}$ per Ga between 3.2 and 1.5 Ga followed with

more gradual ($\sim 1\text{‰}/\text{Ga}$) increase for the past 1.5 Ga. Average $\delta^{18}\text{O}$ values for each binned time interval and for the whole dataset do not correlate with other parameters such as CIA and $\delta^{13}\text{C}_{\text{org}}$ values, but exhibit broad positive correlation with δD values (**Fig. 6b**).

3.3 Low $\delta^{18}\text{O}$ values in 2.45-2.2 Ga shales and some Neoproterozoic shales

We observe a significant, several ‰, downward shift and a decrease in the range of $\delta^{18}\text{O}$ values (7-9‰) in 2.45-2.2 Ga shales that are associated with Paleoproterozoic glaciations (**Figs. 3, 4, 8**). These samples contain abundant micas and have CIA values equal to or higher than the overlying and underlying formations and thus underwent equal or greater degree of chemical weathering (**Tables A1-A2**). Their persistently low $\delta^{18}\text{O}$ values of $8.4 \pm 1\text{‰}$ are ~ 6 to 10‰ lower than those of the pre- and post-glacial shales. This data provides strong evidence of near-to-surface alteration and diagenesis in the presence of ultra-low $\delta^{18}\text{O}$ glacial meltwaters. We further discuss this scenario below. Notably, these units contain almost no organic and inorganic carbon (**Table A1**) and might be weathering products of glacial flour and diamictites under extreme greenhouse conditions soon after their deposition. Analysis of shales associated with Neoproterozoic Sturtian and Marinoan glaciations (Table A2) also shows lower $\delta^{18}\text{O}$ values compared to pre- and post-glacial shales, but CIA values have not been determined for these samples.

3.4 CIA and $\delta^{18}\text{O}$ values

Figure 5a compares bulk rock $\delta^{18}\text{O}$ values with calculated CIA values and demonstrates lack of statistically significant correlation. It is noteworthy that the 2.45-2.2 Ga syn-glacial shales exhibit equal to higher CIA ratios with respect to older or younger Paleoproterozoic shales at lower $\delta^{18}\text{O}$ values. CIA values in shales from our study and those in Condie et al. (2001) and Bahlburg and Dobrzinski (2011) demonstrate no overall trend with age, but a significant scatter from 50 to 100. The average CIA values for each time interval when plotted against the age show zero slope and the average value of $75.5 \pm 8\%$, halfway between fully-weathered (CIA=100) and unweathered (CIA=50) materials. However, the CIA for tillites and

diamictites from our study is lower than for the overlying formations. This is similar to the observations of Young (2013) for the Huronian Lorrain Formation and the underlying diamictites, and results of Bahlburg and Dobrzinski (2011) for the Neoproterozoic tillites. When plotted against age, CIA (**Table A2**) exhibits little change for the past 3.5 Ga with no significant correlation with $\delta^{18}\text{O}$.

3.5. δD values of shales

The δD values of bulk-shale samples (devoid of or corrected for kerogen) range from -85 to -40‰ (**Table A4**). These values are comparable to those for Phanerozoic shales and clays (Sheppard and Gilg, 1996; **Fig. 6**); specifically for less than 50 Ma old, relatively fresh smectites (Mix and Chamberlain, 2014). Similar values were also found in ~3.5 Ga metapelites (Huebner et al. 1986), suggesting constant δD values of shales through time. The same wide range of δD values (-70 to -40‰) is broadly comparable to that of mantle-derived water, crust-derived igneous rocks and is common for meteoric and basinal waters (Taylor and Sheppard, 1986). This overlap makes it hard to distinguish underlying processes and it also suggests that δD values of shales are insensitive to chemical weathering and are not specific to time.

The important exception from this trend in our dataset is the ~2.45-2.2 Ga shales that have lower δD values, reaching to -85‰, and exhibiting positive correlation with $\delta^{18}\text{O}$ values (**Fig. 6b**). As 2.45-2.2 Ga syn-glacial shales contain almost no C_{org} (see **Table A1**), their δD values entirely reflect hydrogen composition of OH^- component of mica. Since typical lacustrine shales deposited under modern climatic conditions are on average 1.4‰ lighter than marine shales (Land and Lynch, 1996), these values suggest near-to-surface exchange with ultra-low δD waters during this time interval that imparted more negative δD values. Bindeman and Serebryakov (2011) reported remarkably negative δD values (-235‰) for rocks interpreted to be highly metamorphosed sediments, which underwent high-T exchange with ultra-low δD glacial meltwaters at 2.4-2.2 Ga.

3.6. Total organic carbon content of shales, $\delta^{13}\text{C}_{\text{org}}$ values, and their correlations

When plotted vs. age (**Fig. 7a**), $\delta^{13}\text{C}_{\text{org}}$ values of our dataset plot along an earlier established trend (Schidlowski 1983; Strauss et al., 1992; Hayes et al., 1999) and reproduce known ~2.6 Ga excursion to low $\delta^{13}\text{C}_{\text{org}}$ values attributed to methanotrophy (Hayes, 1994). $\delta^{13}\text{C}_{\text{org}}$ values do not correlate with the amount of TOC. We observe no correlation between $\delta^{18}\text{O}$ values of bulk shale samples and their $\delta^{13}\text{C}_{\text{org}}$ values (**Fig. 7b**), suggesting decoupling of these two isotopic systems.

3.7. Bulk-shale $\delta^{18}\text{O}$ values through time and correlation with other sedimentary proxies

Fig. 9 compares secular $\delta^{18}\text{O}$ trend for shales with that for carbonates and cherts. While all of them show an increase with decreasing age, we observe important differences in the shape of $\delta^{18}\text{O}$ trends: both the average and particularly the highest 10% of $\delta^{18}\text{O}$ values in shales increase in a concave down pattern (**Figs. 8, 9**), with decelerating increase after ~2.5 Ga. In contrast, the carbonate and chert secular trends have a concave up pattern with accelerated rise starting in the Neoproterozoic. Noticeably, the shale record does not show such a steep increase at 550 Ma (**Fig. 9**) nor further increase in the Phanerozoic, as the Neoproterozoic shales have the same range of $\delta^{18}\text{O}$ values as the Early Paleozoic shales, while the Late Paleozoic shales have even lower values. It is uncertain whether these low values are related to the Early Permian Ice Ages. Overall, there is only rather insignificant $\delta^{18}\text{O}$ increase of 2 to 4‰ for the past 2 Ga based on the average or upper 10% percentile of shales. For shales, unlike for carbonates and cherts, the most dramatic rise occurred at 3.0-2.5 Ga during the Meso- to Neoarchean. Such temporal trend for shales is most comparable in shape with crustal growth curves and Hf and Nd isotope evolution of zircons and sedimentary rocks, respectively, through time explained by rapid crustal growth in the Archean and progressively increasing extent of crustal recycling afterwards (**Fig. 10**; Goldstein and O’Nions, 1981; Jacobsen, 1988; Taylor and McLennan, 1995; Belousova et al., 2010; Hawkeworth et al., 2006).

4. DISCUSSION

Among all the stable isotope systems and chemical parameters studied, we observe meaningful correlation between and temporal changes in $\delta^{18}\text{O}$ and, to a lesser extent, δD values. It is thus important to consider first the meaning of $\delta^{18}\text{O}$ and δD values of bulk shales as 1) a proxy of meteoric water composition during weathering and diagenesis, and 2) effect of crustal recycling on secular trend in these values. In the sections below, we explore the role of climate, evolving $\delta^{18}\text{O}$ composition of seawater, and crustal recycling.

4.1 Meaning of $\delta^{18}\text{O}$ values of shales formed under different climatic conditions in the modern world and comparison with Precambrian shales

From the general principles, $\delta^{18}\text{O}$ values of clay and ambient waters, or their $^{18}\text{O}/^{16}\text{O}$ ratio, R , can be related as:

$$R_c = (\alpha(T) * R_w - R_p) * K + R_p + D, \quad \text{or} \quad (1a)$$

$$\delta^{18}\text{O}_c = (\delta^{18}\text{O}_w + \Delta^{18}\text{O}_{c-w} - \delta^{18}\text{O}_p) * K + \delta^{18}\text{O}_p + D \quad (1b)$$

where $\alpha(T)$ is a fractionation factor between clay minerals and water ($=R_c/R_w \approx \Delta^{18}\text{O}_{c-w} = \delta^{18}\text{O}_c - \delta^{18}\text{O}_w$). P is an isotopic composition of the average crustal protolith undergoing weathering in source area, D is a closed system diagenetic isotopic shift upon lithification that includes, for example, illite-smectite transformation (Clauer et al., 1990) and fractionation associated with pore water expulsion, and K is a degree of chemical ($K=1$) vs. physical ($K=0$) weathering*. The use of ratios R_c and R_w of isotopes instead of $\delta^{18}\text{O}$ values is preferred to linearize non-linear isotopic changes at large $\Delta^{18}\text{O}_{\text{mineral-water}}$, but we use $\delta^{18}\text{O}$ values (Eq 1b) for illustrative purposes and simplicity.

We first accept that changes in $\delta^{18}\text{O}$ values of mudstones in depositional basins are limited

*The K parameter varies with T and thus with latitude and climate. With a decrease in global T or in case of deposition at high latitude, K would approach 0, resulting in lower $\delta^{18}\text{O}_c$ values close to that of unweathered igneous protolith (**Fig. 1**). At high- T , when intensity of chemical weathering is close to 100% and $K=1$, clays will approach oxygen isotope equilibrium with waters.

during diagenesis and lithification based on the observation of little isotopic exchange in recent marine sediments (Savin and Epstein, 1970a, b; Lawrence and Taylor, 1971; Land and Lynch, 1996). δD value could be negative only if $\delta^{18}O$ and δD values of pore waters are ultra low, which is the case for the 2.45-2.2 Ga shales (**Figs. 3-6**).

Oxygen isotope composition of protolith (P) may range from normal- $\delta^{18}O$, igneous values (+5.7 to +7.0‰) to high- $\delta^{18}O$, sedimentary values (+10 to +20‰), and this ratio could change through time and vary in space. We consider that the range of $\delta^{18}O$ values at each time interval is a reflection of the extent of physical vs. chemical weathering, and plot the average and the upper end $\delta^{18}O$ values on **Fig. 9**.

The $\delta^{18}O_w$ and $\alpha(T)$ values in Eq. 1 determine $\delta^{18}O_c$ values of mudstones, and both are function of temperature. Experimental studies of clay-water isotope exchange (e.g., Savin and Lee, 1988) show that α decreases with increasing T , resulting in lower $\delta^{18}O_c$ values under the constant $\delta^{18}O_w$ value. The $\delta^{18}O_w$ is generally taken as the value of mean annual precipitation, $\delta^{18}O_{MAP}$. It decreases with decreasing temperature and increasing latitude and altitude as a reflection of isotopic distillation, and, to a lesser degree, the amount of precipitation. Dansgaard (1964) proposed $\delta^{18}O_{MAP} = 0.69T - 13.6$ relationship for T up to $\sim 18^\circ C$, and a much shallower slope at higher temperatures. Bowen (2008) used $\delta^{18}O_{MAP} = 0.299T - 12.4$ relationship for precipitation based on global mean annual temperature, in line with meridional trend in oxygen isotopes generated by Global Circulation Models (GCM, e.g., Jouzel et al., 2000) for temperatures up to $22^\circ C$. Based on these relationships, the $\delta^{18}O_w$ values are only 1 to 2‰ lower than that of seawater ($\delta^{18}O_{sw}$) in humid coastal environments, such as in tropical Africa and across a wide range of latitudes and temperatures from $+18$ to $+30^\circ C$ (Bowen, 2008). These observations and earlier data in Rozanski et al. (1993) demonstrate significant flattening of the $\delta^{18}O_w$ - T trend above $22^\circ C$, resulting in $\delta^{18}O_c$ value being independent of temperature (**Fig. 1**). Savin and Hsieh (1998) inferred that $\delta^{18}O$ and δD values of kaolinite formed in equilibrium with meteoric waters at T above $+11^\circ C$ are essentially independent of temperature (**Fig. 1**) within the

scatter. Higher T will also likely result in enhanced chemical weathering and higher CIA and K parameters (Fig. 1).

Combined effects of $\delta^{18}\text{O}_w(T)$ and $\alpha(T)$ compensate each other (as is shown on **Fig. 1** and explained above), resulting in maximum equilibrium $\delta^{18}\text{O}_c$ values for authigenic product. Net outcome of surface temperature increase from 0° to +22°C would result in 5-6‰ rise in $\delta^{18}\text{O}_c$, but above ~20°C $\alpha(T)$ values decrease resulting in lower $\delta^{18}\text{O}_c$.

Although not considered by previous researchers, more extreme climatic conditions, such as those in the aftermath of Snowball Earth, known as the hot-house conditions (Hoffman and Schrag, 1998), with the hypothetical temperatures of +50 to +80°C, would result in a smaller $\alpha(T)$ value, generating clays with ~2-3‰ lower $\delta^{18}\text{O}_c$ values than the maximum possible values (**Fig. 1**). The closest Cenozoic analogue for the Precambrian hot-house climate conditions is the Paleocene-Eocene Thermal Maximum, when there was no land ice present, and GCM and isotopic and chemical proxies such as $\delta^{18}\text{O}$ values of foraminifera and Mg/Ca ratios of carbonate suggest that the mean annual temperature in tropics was >30°C and sea surface temperatures were +30 to +32°C across low and middle latitudes (Huber and Caballero 2011; Lunt et al. 2012) and +10°C at high latitudes. Due to these higher T and significantly reduced meridional gradients in seawater temperatures, $\delta^{18}\text{O}_c$ values would be lower and more uniform across different latitudes and weathering product should contain greater authigenic component (K>1). Furthermore, 1 to ~4‰ lighter $\delta^{18}\text{O}$ values of seawater under ice-free conditions (Herwartz et al. 2015) would enhance the effect. Similarly, in ice-free world, when all continents are near the equator as was likely the case during the early Paleoproterozoic (cf. Evans and Pisarevsky, 2008), oxygen isotope values of seawater should be similarly lower.

In conclusion, wide ranges of $\delta^{18}\text{O}$ in each time interval in the Precambrian are expected and suggest diversity of climatic conditions, similar to the Phanerozoic world. Negative $\delta^{18}\text{O}$ excursions are expected during hothouse conditions with a smaller range of values. Snowball conditions would result in stronger depletion in ^{18}O . Besides these climatic controls, the long-term trend of increasing $\delta^{18}\text{O}$ values of the average shale is linked below to crustal maturation.

4.2. Crustal evolution trend: Sequestration of ^{18}O through time

Temporal evolution of average $\delta^{18}\text{O}_{\text{shale}}$ values can be modeled with the following mass balance equations including oxygen isotope values of supracrustal rocks ($\delta^{18}\text{O}_s$) and juvenile igneous rocks ($\delta^{18}\text{O}_i = +6\text{--}+7\text{‰}$) as crustal components, and the isotope effect of ^{18}O gain due to chemical weathering during each time interval, $\Delta^{18}\text{O}$:

$$\delta^{18}\text{O}_{\text{shale}} = \delta^{18}\text{O}_{\text{crust}} + \Delta^{18}\text{O}_{\text{crust-water}} \quad [2]$$

$$\text{where } \Delta^{18}\text{O}_{\text{crust-water}} = K * (\delta^{18}\text{O}_c - \delta^{18}\text{O}_w) \quad [3]$$

$$\delta^{18}\text{O}_{\text{crust}} = \delta^{18}\text{O}_s * X + \delta^{18}\text{O}_i * (1 - X) \quad [4]$$

where X is the mass proportion of supracrustal rocks vs. juvenile igneous rocks exposed and undergoing weathering during the considered time interval of deposition. Last parameter in Eq. 2 is a latitude-averaged isotopic fractionation, modulated by the intensity of physical vs. chemical weathering (K in Eq. 1). While quantification of these equations is hampered by the unknown input parameters, we infer below that the increase in $\delta^{18}\text{O}_{\text{shale}}$ values with time is a direct result of the shift in $\delta^{18}\text{O}$ values of the exposed crust, $\delta^{18}\text{O}_{\text{crust}}$, that undergoes weathering. This is in turn a function of X, a largely unknown, but doubtlessly geographically and temporally variable parameter, which is likely a function of crustal generation vs. destruction, linked to plate tectonics*. Our temporal trend of $\delta^{18}\text{O}_{\text{shale}}$ values can be compared with proposed crustal growth models (**Figs. 8, 10**) since oxygen constitute 50% of the crust. The data permits the following observations. First, the average $\delta^{18}\text{O}_{\text{shale}}$ value steadily increases with time, which fits to either a straight line ($R^2=0.93$) or a concave down second-order polynomial ($R^2=0.96$).

The flattening trend of the highest $\delta^{18}\text{O}$ values of the Late Proterozoic to early Phanerozoic

* Weathering of crust would result in sequestration of ^{18}O into the shale reservoir, which is not easily subducted or delaminated into the mantle as it is deposited on continental margins and trapped in accretionary prisms. Concave down trend suggests that production of high- $\delta^{18}\text{O}$ continental crust reached a steady state with respect to addition of juvenile crust by the Late Archean. In this model, the juvenile crust being ^{18}O -depleted is getting progressively enriched in ^{18}O once it is exposed to weathering.

shales is better fitted to the second-order polynomial. Second, there are distinct negative and positive $\delta^{18}\text{O}_{\text{shale}}$ excursions ranging in magnitude up to several ‰, which are reflected in both the average and the highest $\delta^{18}\text{O}_{\text{shale}}$ values. We interpret the first-order trend as evidence for progressive sequestration of ^{18}O -enriched material into the growing continental crust, through the secular increase in the relative ratio of weathering-influenced supracrustal deposits in the continental crust, X , in Eq. 4.

Expectedly, each time interval has a wide range of $\delta^{18}\text{O}_{\text{shale}}$ values from the juvenile igneous (mantle-like) to high- $\delta^{18}\text{O}$ values, but younger periods have both higher average and maximum $\delta^{18}\text{O}_{\text{shale}}$ values (**Fig. 8**).

The steeper rise of $\delta^{18}\text{O}_{\text{shale}}$ value in the first half of Earth's history is consistent with the faster initial crustal growth as is suggested by Nd and Hf model ages and crustal residence time of sediments and zircons (**Fig. 10**; Jacobsen, 1988; Taylor and McLennan, 1995; Belousova et al., 2010; Hawkesworth et al., 2006). We suggest that the faster initial rise in $\delta^{18}\text{O}$ values of shales might be related to a higher preservational potential of upper crustal components with high- $\delta^{18}\text{O}$ values on the hotter Earth with plume-related or incipient plate tectonics where delamination of crustal roots with low- $\delta^{18}\text{O}$ values has been inferred (Taylor and McLennan, 1985; Condie and O'Neill, 2010) and numerically modeled (e.g., Gerya, 2014; Johnson et al., 2014). This delamination of low- $\delta^{18}\text{O}$ roots might have been more effective than sequestration after the onset of plate tectonics that lead to partial sediment recycling.

The $\delta^{18}\text{O}$ zircon record through time (Valley et al. 2005; Hawkesworth et al. 2010) also exhibits progressive increase in the range and the average of oxygen isotope values starting from ~2.5 to 2.0 Ga, and scarcity of high- $\delta^{18}\text{O}$ zircons prior to that. The upper 10% percentiles of oxygen isotope data for zircons are plotted on **Fig. 8** vs. time. These are, for example, ~10-10.5‰ at 0.55 Ga and ~8‰ at ~2 Ga. The $\Delta^{18}\text{O}_{\text{shale-zircon}}$ value is increasing with the decreasing age. If shale with 60 wt% SiO_2 melted and zircon crystallized from this magma, the fractionation factor would be $\sim 1.5 \pm 0.5$ ‰ depending on the temperature and magma composition (e.g., Lackey et al., 2008). This comparison indicates that zircons have too low

$\delta^{18}\text{O}$ values to be in equilibrium with shales; an observation that can be easily reconciled considering that zircons did not crystallize from melts derived solely from shales or even from remelted sedimentary rocks, but rather from their mixture with basaltic differentiates having juvenile, mantle-like $\delta^{18}\text{O}$ value of $\sim 5.7\text{‰}$. In this context, bulk-sample oxygen isotope analysis of shales from geochronologically well-constrained formations is a better and more direct proxy for the evolving crust than that of zircons.

4.3. Wilson Cycle and $\delta^{18}\text{O}_{\text{shale}}$ Secular Trend

Variations in $\delta^{18}\text{O}_{\text{shale}}$ values, and in particular second-order rises and falls in the temporal record (**Fig. 8a**) might be linked to the supercontinent (Wilson) cycle. We find that high- $\delta^{18}\text{O}_{\text{shale}}$ values (with respect to the secular trend curve) are characteristic for the Late Cenozoic, Late Proterozoic (0.9-0.75 Ga), and Late Archean (2.5-2.7 Ga) time intervals, while low- $\delta^{18}\text{O}_{\text{shale}}$ values are characteristic for the Carboniferous-Jurassic (0.15-0.35 Ga) and Mid-Paleoproterozoic (2.15-1.8 Ga). The first-order supercontinent cycle, through its amplifying effect on isotopic composition of meteoric waters and weathering (e.g., **Fig. 1**), might explain this pattern as qualitatively suggested by considering the following genetically-plausible cause-and-effect relationships.

1) *Climate changes* due to landmass distribution and total land mass area and associated effect on $\delta^{18}\text{O}_w$ values:

1a) Supercontinent => drier and overall colder continental interior climate conditions with a potential for continental glaciation => lower- $\delta^{18}\text{O}$ composition of precipitation => low and highly variable $\delta^{18}\text{O}$ values of weathering products (see Fig. 1).

The opposite of that is:

1b) Widely dispersed continents => maritime (warmer, more stable) climate conditions => high and less variable $\delta^{18}\text{O}$ values of weathering products.

2) *Tectonic and Provenance control*: breakup (spreading) vs. assembly (mountain building) of the supercontinent cycle and their effects on $\delta^{18}\text{O}$ values of bulk weathering product.

2a) Breakup of the supercontinent, extensive submarine spreading environments, absent or scarce collisional settings => less juvenile crust exposed subaerially => weathering and recycling of old continental crust => high $\delta^{18}\text{O}$ values of weathering products.

The opposite of that is the supercontinent assembly:

2b) convergence of continents => weathering of juvenile low- $\delta^{18}\text{O}$ crust of active arcs => production, followed by accretion, of sedimentary prisms with normal to low- $\delta^{18}\text{O}$ composition of continental and island arc-derived sediments, and, finally, continent-continent collisions => large range of $\delta^{18}\text{O}$ values with upsection trend towards higher $\delta^{18}\text{O}$ values.

These tectonic and climatic effects might be relevant to explain low $\delta^{18}\text{O}$ values of the 1.05 Ga and 0.3 Ga shales corresponding to the tenure of two supercontinents, Rodinia and Pangea (**Fig. 8a**). The steep rise of $\delta^{18}\text{O}$ values in shales corresponds with periods of the supercontinent breakup and independently drifting continents: at present and at 0.8 and 1.5 Ga, in line with the discussion above. However, the lowest $\delta^{18}\text{O}$ values are in shales with ages between 2.45 and 2.2 Ga and 0.65-0.75 Ga, which correspond to the Huronian glacial epoch (see section 4.5) and Neoproterozoic glaciations.

4.4. Preferential ^{18}O -scavenging into the continental crust vs. secular evolution of the hydrosphere?

An alternative interpretation of increasing $\delta^{18}\text{O}_{\text{shale}}$ values with time is an overall rise in the $\delta^{18}\text{O}$ values of seawater, affecting the entire hydrologic cycle, including meteoric water $\delta^{18}\text{O}_{\text{w}}$ (Eq. 1) values and, consequently, $\delta^{18}\text{O}_{\text{clay}}$ values. The $\delta^{18}\text{O}$ values of chemical and biogenic precipitates, such as carbonates and phosphates, might record $\delta^{18}\text{O}_{\text{w}}$ value of the hydrosphere and temperature of the oceans. Reasons why their $\delta^{18}\text{O}$ values progressively decrease with increasing age (**Fig. 9**) have been hotly debated to reflect lower $\delta^{18}\text{O}_{\text{sw}}$, higher T, a combination of the two, changes in low- and high-T hydrothermal fluxes, or more intense post-depositional alteration of older carbonates (**Fig. 9**, Veizer et al., 1992; Wallmann et al., 2004; Gregory, 1991;

Muehlenbachs and Clayton, 1976; Muehlenbachs, 1998; Holland, 1984; Kasting et al. 2006; Jaffres et al., 2007; Frank and Lyons, 2010). Similar trend is also shown by the Precambrian cherts that have lower $\delta^{18}\text{O}$ values than Phanerozoic cherts (**Fig. 9**, Perry and Tan, 1972; Perry and Ahmad, 1982; Knauth and Lowe, 2003).

When carbonate and chert records are plotted along with that of shales (**Fig. 9**), both carbonates and cherts show steeper overall increase in $\delta^{18}\text{O}$ values than shales: carbonates (6.3‰ / Ga), cherts (4.7‰ / Ga), and shales (2.1‰ / Ga).

4.6. Origin of the 2.45-2.2 Ga low- $\delta^{18}\text{O}$ shales

The important discovery of this study is that shales associated with the Paleoproterozoic glacial periods have universally low- $\delta^{18}\text{O}$ (and low- δD) values, which are the lowest of all the shales studied so far (e.g., Land and Lynch, 1996; Lawrence and Taylor, 1972; Savin and Epstein 1970). Same trend is preliminarily observed for the Neoproterozoic. The +7 to +10‰ oxygen isotope values that we measured could in theory represent unweathered igneous source, however since the studied samples contain large amounts of authigenic clays (based on our XRD investigation) and have CIA values similar to or even higher than other studied shales (**Fig. 5a**), this is not the case. δD values of these shales are also low and positively correlate with $\delta^{18}\text{O}$ values (**Fig. 6b**), reinforcing glacial melt water interpretation. Notably, these units contain almost no organic or inorganic carbon (**Table A1**) and might be weathering products of glacial flour and diamictites under extreme greenhouse conditions soon after their deposition. Thus, this data provides strong evidence of near-to-surface alteration and diagenesis under one or both of the following conditions: 1) formation at higher temperature, resulting in a smaller $\Delta^{18}\text{O}_{\text{clay-water}}$ fractionation factor and lighter $\delta^{18}\text{O}$ clay product, 2) diagenesis of these shales in lacustrine, deltaic or shallow-marine environments (e.g. sikussak, Fig. A1) influenced by ultra-low $\delta^{18}\text{O}$ (ca. -35-45‰) glacial meltwaters coming from Huronian glaciers. In the latter scenario, the diagenetic shift, D parameter, in Eq 1 is negative and, likely, several permil in magnitude, at any temperature. The synglacial Makganyene shales of South Africa were

deposited in marine environment and they have slightly higher $\delta^{18}\text{O}$ values ($13\pm 0.8\text{‰}$) than any other non-marine shales in this age group. This can be explained by a positive diagenetic shift in contact with seawater having higher $\delta^{18}\text{O}_{\text{sw}}$ values.

The envisioned paleogeographic reconstruction for deposition of these synglacial shales is that of the sikussak-type environment illustrated on **Fig. A1**, where glacial tillites and flower were delivered by glaciers and deposited. Following deglaciation, further weathering and diagenesis of these deposits proceeded in the presence of ultra-low $\delta^{18}\text{O}$ glacial meltwaters in either lacustrine or shallow-marine environments, similar to those in today's glaciated regions.

4.7. $\delta^{18}\text{O}$ and CIA values before and after the Great Oxidation Event

With the exception of a negative shift in $\delta^{18}\text{O}$ values (at nearly constant CIA values) in 2.45-2.2 Ga and Neoproterozoic shales, we observe no obvious change across the GOE in either $\delta^{18}\text{O}$ or CIA values (Fig. 5), suggesting that weathering cycle has not changed dramatically despite the long-term decrease and fluctuations in CO_2 , appearance of atmospheric oxygen, and notable changes in Fe oxidation state in shales, disappearance of detrital sulfides and uraninite, and atmospheric CH_4 fluctuations (e.g., Bekker and Holland, 2012; Bekker, 2015). The existence and the role of microbial life in Precambrian soils is a highly debated topic (Retallack, 2001; 2007), therefore weathering intensity could have been compensated by a different microbe populations and enzymes. One possibility is that with the appearance of atmospheric oxygen, methane in the atmosphere could have been replaced with CO_2 to maintain greenhouse conditions to compensate for lower solar luminosity (cf. Bekker and Kaufman, 2007). The observation of an increase in $\delta^{18}\text{O}$ values in shales through time, despite higher inferred Precambrian CO_2 concentrations (e.g. Holland, 1984; Kasting et al., 2006; Sheldon, 2006), and thus potentially higher H_2CO_3 production and intensity of carbonic acid weathering, suggests, if anything, lack or the opposite connection between long-term averaged CO_2 concentrations in

the atmosphere and $\delta^{18}\text{O}_{\text{shale}}$ values, confirming our conclusion that it is the crustal evolution that primarily controls sequestration of ^{18}O with time.

5. Conclusions

1) We observed an increase in $\delta^{18}\text{O}$ values of shales through the past 3.5 Ga with a decelerating trend after the late Neoproterozoic. This pattern is different from the coeval trends of carbonates and cherts, in which $\delta^{18}\text{O}$ values rise sharply after the Neoproterozoic.

2) This temporal trend in shales is explained by the combined effects of progressive crustal maturation and sequestration of high- $\delta^{18}\text{O}$ weathering products in the upper crust. On Early Earth delamination of low- $\delta^{18}\text{O}$ continental roots might have been more effective than sequestration after the onset of plate tectonics that led to partial sediment recycling. Second and third order $\delta^{18}\text{O}$ fluctuations are linked to the supercontinent cycle.

3) We discovered that the lowest $\delta^{18}\text{O}$ and δD values in shales are associated with Paleoproterozoic and, potentially, Neoproterozoic glaciations and link these values to interaction with glacial meltwaters.

4) We observed no difference in $\delta^{18}\text{O}$ values in shales deposited before and after the GOE, suggesting no stepwise change in weathering intensity.

5) Binned time intervals have wide ranges in $\delta^{18}\text{O}$ values reflecting diversity of climatic and weathering conditions.

6) Despite increasing $\delta^{18}\text{O}$ values there is no temporal CIA trend suggesting that on the average, it is the sequestration of ^{18}O and not intensity of chemical weathering that controls increasing $\delta^{18}\text{O}$ values through time.

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$\delta^{13}\text{C}_{\text{org}}$, and TS data. We thank two anonymous reviewers and Greg Retallack for helpful reviews and comments.

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Figure Captions

Fig. 1. Schematic explanation for oxygen isotope values in shales.

Oxygen isotope values of clay minerals, secondary quartz and bulk shale as a function of temperature and $\delta^{18}\text{O}$ values of precipitation. Calculated $\delta^{18}\text{O}$ values of clay minerals (smectite-illite) formed in a complete equilibrium with mean annual precipitation for the modern world ($\delta^{18}\text{O}_{\text{sw}} = 0\text{‰}$, precipitation data as a function of mean annual temperature is taken from Rozanski (1993), clay mineral-water isotope fractionation is from Savin and Lee (1988), quartz-water isotope fractionation is from Kawabe et al. (1978), kaolinite data is taken from Savin and Hsieh (1998). We used the second-order polynomial approximation of $\delta^{18}\text{O}_{\text{w}}$ values vs. temperature from Rozanski et al. (1993) for temperatures ranging from 0° to $+32^\circ\text{C}$ resulting in -1.8‰ value of mean annual precipitation at $+32^\circ\text{C}$. For higher than $+32^\circ\text{C}$ local mean annual temperature, we assumed a constant -1.8‰ $\delta^{18}\text{O}_{\text{w}}$ value as rainwater sources at this temperature range would be dominated by massive monsoons with little oxygen isotope fractionation. Chemical Index of alteration (CIA, Nesbitt and Young, 1982) is shown and is 50 for physical weathering only ($K=0$, Eq.1 in text) and 100 for full chemical weathering ($K=1$). Bulk shale, which is a mixture of detrital and autigenic components, will likely evolve from $K=0$ to $K=1$ as is shown by the dashed line, through an exemplary point $K=0.45$. See text for the detailed discussion.

Fig. 2. Correlation of $\delta^{18}\text{O}$ values of bulk shales with $\delta^{18}\text{O}$ values of clay minerals (a) and XRD-determined quartz content (b).

a) Correlation between $\delta^{18}\text{O}$ values of clay portion and bulk shale for Phanerozoic and Precambrian shales plotted from Table 1 of Land and Lynch (1996). Note good linear correlation and that the bulk shale data is only $\sim 1\text{‰}$ higher than $\delta^{18}\text{O}$ values of clay component (due to authigenic quartz), implying that bulk shale analysis is an appropriate method for paleoenvironmental studies.

834 b) $\delta^{18}\text{O}$ values of shales vs. XRD-determined % of quartz from this work and that of Land and
835 Lynch (1996). Note lack of correlation, the same result is also obtained for the whole-
836 rock clay fraction; not shown, suggesting that it is not the content of quartz that
837 determine $\delta^{18}\text{O}$ values of bulk shale, but a reflection of weathering process that formed
838 the shales.

839 **Fig. 3.** Histograms of published $\delta^{18}\text{O}$ data for Phanerozoic and Precambrian shales through time.

840 a) Literature data (left column) and our newly generated dataset for Precambrian shales (right
841 column). Note that Archean and Paleoproterozoic shales have overall lower $\delta^{18}\text{O}$ values than
842 their Phanerozoic counterparts, but have equally large spread of $\delta^{18}\text{O}$ values at each time
843 interval. Sources of literature data: Land and Lynch, 1996; Masuda et al., 1992; Pokrovskii
844 and Vinogradov, 2001, Savin and Epstein, 1970b; Viswanathan, 1977; Longstaffe and
845 Schwarcz, 1977.

846 b) Comparison of Huronian syn-glacial shales with pre- and post-glacial shales. Note that shales
847 associated with the inferred Snowball Earth episodes of the Paleoproterozoic age have
848 particularly low $\delta^{18}\text{O}$ values.

849 **Fig. 4** Oxygen isotope evolution of shales in time based on this work and previously published
850 data.

851 **Fig. 5.** Chemical Index of Alteration (CIA) and oxygen isotope values for shales from this work
852 and published literature data.

853 a) $\delta^{18}\text{O}$ values vs. CIA for syn-, pre-, and post-glacial shales.

854 b) CIA vs. age and comparison with Nesbitt and Young (1982) end-members.

855 **Fig. 6.** Hydrogen isotope data for silicate fraction of bulk shales with the emphasis on the
856 Archean-Paleoproterozoic transition.

857 a) Temporal trend. Note that the overall range for the Precambrian shales is comparable to
858 that of the Phanerozoic shales, with the exception of 2.45-2.2 Ga shales that are
859 associated with the Huronian glaciations.

b) Oxygen vs. hydrogen isotope scatter graph. Note positive correlation interpreted to reflect ultra-low- δD values of glacial meltwaters during the Huronian glaciations.

Fig. 7. The $\delta^{13}C$ values for organic carbon in shales through time.

a) $\delta^{13}C_{org}$ vs. age, based on this work and compiled literature data (squares - Strauss et al., 1992; triangles - Hayes et al., 1999); dashed lines indicate timing of the Huronian and Neoproterozoic Snowball Earth glaciations.

b) $\delta^{13}C_{org}$ vs. $\delta^{18}O$ values for shales with different ages showing no correlation (data is from the Supplementary Materials Table 1).

Fig. 8. Evolution of the average $\delta^{18}O$ values of shales (red squares) and the three highest $\delta^{18}O$ values (blue diamonds) through time. Note decelerating growth of $\delta^{18}O$ values with the decreasing age and a steeper increase before 2.5 Ga. The highest $\delta^{18}O$ zircon values defining the upper bound of the range for zircons (data are from Valley et al., 2005) are shown for comparison to demonstrate difference from the trend of $\delta^{18}O_{shale}$ values, see text for further discussion.

a) Comparison with the supercontinent cycles and $\delta^{18}O$ values of zircons. Arrows indicate variations due to the supercontinent cycle and glaciations and are further discussed in the text.

b) Time binned averages, long-term evolution, and best-fit parameters for the average (red squares) and the three highest (blue diamonds) $\delta^{18}O_{shale}$ values through time with the data for synglacial shales excluded. Note progressive increase in $\Delta^{18}O_{shale-zircon}$ ($=\delta^{18}O_{shale} - \delta^{18}O_{zircon}$), see text for the further discussion. Modern sediments are from Land and Lynch, 1996 (low values) and estimates of Savin and Epstein, 1970b (high values).

Fig. 9. Comparison of $\delta^{18}O$ values of shales with those for carbonates and cherts. a) temporal trends. Note significant difference in the shape of trends – concave down for shales and concave up for carbonates and cherts, and that the slope increases from shales to cherts and to carbonates. b) Statistically-weighted difference between shales carbonates and cherts with the averaging temporal window that has comparable number of analyses. Note increasing

887 divergence in Phanerozoic, explained by increasing $\delta^{18}\text{O}$ values of carbonates and cherts but
888 not shales, and a negative excursion during 2.2-2.4 Ga glaciations explained by lower $\delta^{18}\text{O}$
889 values of shales, but not carbonates and cherts.

890 **Fig. 10.** Models for the crustal growth over time with the superimposed curve of $\delta^{18}\text{O}$ values for
891 shales emphasizing increase in crustal recycling through time leading to sequestration of
892 high- $\delta^{18}\text{O}$ component into the continental crust.

SHALES THROUGH TIME

Fig. 1

Fig. 2

Fig. 3a

Fig. 3b

Fig. 4

Fig. 5a

Fig. 5b

Fig. 6

Fig. 7a

Fig. 7b

Fig. 8a

Fig. 8b

Fig. 9

Fig. 9b

Fig. 10