Three Billion Year Secular Evolution of the Triple Oxygen Isotope Composition of Marine Chert

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Highlights:

- Chert samples from the last 3.4 Gyr yield a secular evolution of $^{18}O/^{16}O$ and $^{17}O/^{16}O$
- Cherts since the Ordovician formed in water with $^{18}O/^{16}O$ and $^{17}O/^{16}O$ close to modern seawater
- Precambrian cherts formed in different fluids or in different diagenetic environments

Abstract: The $^{18}O/^{16}O$ ratios of ancient marine minerals show a puzzling increase over geologic time. Long-term changes in temperature, seawater $^{18}O/^{16}O$ ratios, and post-depositional overprinting can all explain this trend, but few tracers can distinguish between these scenarios. Here, we report high-precision $^{18}O/^{16}O$ and $^{17}O/^{16}O$ ratios of cherts through 3.4 Ga of Earth′s history. We find that Phanerozoic cherts are consistent with having formed in porewaters that are isotopically indistinguishable from modern (ice-free) seawater. In contrast, Precambrian cherts require either formation in waters isotopically distinct from Phanerozoic seawater, or a different mode of formation. If the early diagenetic formation pathway of Precambrian cherts resembles that of Phanerozoic cherts, and the Precambrian cherts are unaltered, then the results would imply that the oxygen-isotope composition of seawater has evolved on billion-year timescales before reaching its present composition by the Ordovician. Under this interpretation it is estimated that seawater had $\delta'^{18}O < -11‰$ at 3.41 Ga, with surface temperatures < 34°C. Although this scenario provides the simplest explanation for the observed $^{18}O/^{16}O$ trend of marine minerals, other scenarios which do not require a secular change in seawater $^{18}O/^{16}O$ cannot be ruled out.

1.1 Introduction:

The oxygen isotope composition of seawater is buffered over geologic time by a balance of high- and low-temperature interactions with the silicate Earth (Gregory and Taylor, 1981; Muehlenbachs, 1998; Muehlenbachs and Clayton, 1976). These interactions have likely confined the $^{18}O/^{16}O$ ratio in seawater to within a small range over the Phanerozoic (i.e. linearized notation: $\delta'^{18}O = \ln[\delta^{18}O+1] = 0 \pm 2‰$ relative to VSMOW) (Coogan et al., 2019; Cummins et al., 2014; Henkes et al., 2018). High-temperature interactions, such as those at seafloor hydrothermal systems, tend to increase seawater $\delta'^{18}O$ values, while low-temperature interactions with oceanic and continental crust tend to lower seawater $\delta'^{18}O$ values. Yet, details of how this seawater buffering system operated for early Earth are unknown. The evolution of seawater $\delta'^{18}O$ may offer clues to the evolution of the solid Earth over geologic time (Jaffrés et al., 2007; Kasting et al., 2006). Changing subaerial exposure of mid-ocean ridges, penetration depths of seafloor hydrothermal circulations, effective seafloor spreading rates, and the spatial extent of volcanic plateaus can all affect seawater $\delta'^{18}O$ values by altering the proportions of high- and low-temperature water-rock interactions at the global scale (Jaffrés et al., 2007; Kamber, 2010; Kasting et al., 2006).

Compilations of data for marine carbonates, phosphates, shales and cherts all show a secular increase in $\delta'^{18}O$ values over Earth history (Bindeman et al., 2016; Levin et al., 2014; Veizer et al., 1997). The oldest minerals show $\delta'^{18}O$ values that are as much as 15‰ lower than their modern equivalents. While a secular evolution of seawater $\delta'^{18}O$ can explain this trend, the explanation is not unique: the $\delta'^{18}O$ data are also compatible with scenarios invoking ≥70°C Earth-surface cooling since the Archean (Knauth and Epstein, 1976; Knauth and Lowe, 2003; Levin et

al., 2014; Perry and Lefticariu, 2014) or progressive alteration of marine minerals in meteoric waters as they age (Levin et al., 2014; Perry and Lefticariu, 2014). This lack of uniqueness has persisted since the first oxygen-isotope measurements of Archean cherts were reported over 50 years ago (Perry, 1967) because $\delta'^{18}O$ values alone cannot distinguish between changes in the isotopic composition of the source water and changes in growth temperature. Clumped-isotope approaches have emerged as a tool to constrain these quantities independently, but their compositions in Precambrian carbonates have likely been altered by heating associated with burial and exhumation (Henkes et al., 2018; Passey and Henkes, 2012; Stolper and Eiler, 2015). Other approaches have been developed, such as $\delta'^{18}O$ values in occluded kerogen (Tartèse et al., 2017), but the degree and nature of alteration in these archives is poorly known. Thus, the idea of a long-term evolution in seawater $\delta'^{18}O$ values remains controversial.

We hypothesize that $^{18}O/^{16}O$ and $^{17}O/^{16}O$ isotope ratios of cherts—i.e., their triple oxygen-isotope composition—can constrain the $\delta'^{18}O$ of ancient porewaters. Ultra-high-precision oxygen triple-isotope measurements (quantified as $\Delta'^{17}O = \delta'^{17}O - 0.5305 \times \delta'^{18}O$) allow one to probe the $\delta'^{18}O$-$\Delta'^{17}O$ relationships between phases, which are bounded by physical-chemical constraints (Cao and Liu, 2011; Hayles et al., 2018; Hayles et al., 2017). For a given source-water $\delta'^{18}O$ and $\Delta'^{17}O$ value, only a bounded range of chert compositions are possible at equilibrium (Hayles et al., 2018; Sharp et al., 2016; Wostbrock et al., 2018). Similarly, the oxygen triple-isotope composition of a given chert is only consistent with a narrow set of growth waters. The low permeability and low oxygen diffusivity in microquartz cherts render them an ideal phase to analyze these variations because they are resistant to alteration once the crystalline quartz phase has formed (Knauth, 1994): experimental measurements of oxygen diffusion rates in grain boundaries of natural chert

samples suggest it would take 30-300 Gyr for exchange to occur across a one-centimeter-thick layer at 450°C (Farver and Yund, 1991).

Earth-system evolution models that predict lower seawater $\delta'^{18}O$ values early in Earth′s history require a lower ratio of high-temperature to low-temperature water-rock interactions in Earth's deep past (Jaffrés et al., 2007; Kasting et al., 2006; Wallmann, 2004). An empirically constrained model for seawater $\Delta'^{17}O$, based on the long-term water-rock mass balance formalism of Muehlenbachs (1998), predicts higher seawater $\Delta'^{17}O$ values when $\delta'^{18}O$ values are low (Pack and Herwartz, 2014; Sengupta and Pack, 2018).

To date, triple-oxygen compositions of only one set of Precambrian (2.5 Ga) and Phanerozoic cherts has been published (Levin et al., 2014). Their compositions show no coherent pattern, but are generally lower in $\Delta'^{17}O$ than expected for equilibrium with seawater at a given $\delta'^{18}O$ value. Closed-system hydrothermal alteration was suggested as a potential driver of triple-oxygen variability in the rock record, although one Phanerozoic chert (~65 Ma Stevns Klint chert) was found to be unaltered (Sengupta and Pack, 2018). Given the sparsity of chert triple-oxygen data, it is not known if the secular evolution in $\delta'^{18}O$ values is also present in $\Delta'^{17}O$ values. If the secular evolution in chert $\delta'^{18}O$ values is mirrored in their $\Delta'^{17}O$ values, chert oxygen-isotope compositions may be diagnostic of changing Earth-system processes through Earth history.

In this study, we expanded the record of triple-oxygen isotopes in chert by analyzing the compositions of suite of marine cherts from the Archaean to late Phanerozoic. Higher $\Delta'^{17}O$ values in ancient cherts, together with oxygen triple-isotope compositions that are incompatible with growth in a modern ice-free ocean, would imply that the $\delta'^{18}O$ value of diagenetic fluids—and perhaps seawater—has evolved over Earth history. Chert compositions compatible with growth in modern-like diagenetic fluids (i.e. seawater) through Earth history would imply robust proportions

of global seawater-rock interactions and relatively constant diagenetic environments for marine chert formation amidst a cooling lithosphere and evolving tectonic boundary conditions.

2. Materials and Methods:

2.1 Materials

Chert samples for this study were taken from units covering 3.4 billion years of Earth's history from three modern day continents. Samples for this study were taken from the Monterrey/Sisquoc Formation (Miocene) of California, San Andres Limestone (Permian) and Onate formation (Devonian) of New Mexico, Caballos Novaculite (Devonian) and Ellenberger Group (Ordovician) of Texas, Liuchapo Formation (Ediacaran) of China, Gunflint Formation (1.880 Ga) in Ontario and the Frisco Formation (2.521 Ga), Moodies Group (3.22 Ga), Mendon Formation (3.258 Ga) and Kromberg Formation (3.41 Ga) of South Africa. Specific localities, references for the samples, GPS coordinates, where known, and some further sample information can be found in Table S1 in the supplemental. Samples are selected based on purity because the analytical technique for oxygen isotopes cannot discriminate between the silica component of chert and detrital components. All samples have been analyzed by LA-ICPMS to verify purity is greater than 98% SiO_2, but the results for only a subset of these samples are presented in the supplemental with the remainder to be presented at a later date.

2.2 Methods

Oxygen isotope analyses were conducted at Rice University using techniques previously described (Yeung et al., 2018). Prior to oxygen isotope analysis, 2-3 mg chert samples and silicate standards are loaded onto a sample plate made of 316L steel. The sample plate is then placed into a cell in the laser fluorination line equipped with a ThF_4 coated ZnSe window. The cell is evacuated to high vacuum using a turbo pump and an infrared lamp is used to heat the sample plate through the window. The heating and pumping are continued until the pressure measured at the pump reads $<10^{-6}$ mbar. When all samples are individual grains, this heating step typically lasts for 3 days, but can take up to a week if hydrous (e.g. opal) or powdered samples are loaded. At the end of this step, the cell containing the samples is filled with ~30mbar of pure F_2 gas generated by heating of a potassium fluoronickelate salt (Asprey, 1976). The purity of the F_2 gas, and in particular the lack of O_2, is verified using periodic F_2-only blank tests mimicking the fluorination procedure but lacking the laser heating step. The samples and standards are exposed to the fluorine gas atmosphere at room temperature for two days. This prefluorination step is done to remove any further traces of moisture from the samples but in no instance was an O_2 yield from this step observed.

Oxygen from silica samples and silicate standards are converted to O_2 gas by reaction with a two-fold excess of purified F_2 gas. Typical operating pressure of F_2 is 60 mbar. Heat for the reaction is provided by a 10.6 μm CO_2 laser (Synrad 48-2; 25W). Reaction temperatures are unknown, but the majority of the reaction proceeds above the melting temperature of the silicates and yields are complete. For all chert samples, no residues remained in the cell after fluorination indicating the samples were composed of pure silica as most common metal fluorides are solids under the reaction conditions. The purity of the silica was confirmed for the samples which LA-ICPMS and electron microprobe analyses were performed (see Supplemental Information). The

resulting gas mixture of F_2, O_2, SiF_4 and trace impurities (e.g. CF_4, NF_3) is first purified cryogenically at -196°C to remove SiF_4 and any other condensable reaction products (e.g. trace CF_4). This is followed by reaction of the F_2 with KBr held at 215°C and condensation of the products at -196°C. The resulting roughly purified O_2 is collected onto a U-trap filled with silica gel and forwarded through a 3.05 m × 1/8" OD gas chromatography (GC) column filled with molecular sieve 5A (80/100 mesh) in a 20 mL/min flow of He carrier gas to remove any trace NF_3. Beginning at ~2 minutes after introduction and ending 10 minutes after introduction, the purified O_2 is recollected in a second silica gel filled U-trap. All processes after the fluorination reaction are automated in order to reduce user-derived variability therein.

The resulting purified O_2 is analyzed for triple oxygen isotope composition on a Nu Instruments *Perspective IS* mass spectrometer (PS001) equipped with a dual inlet and directly connected to the fluorination line. Oxygen gas is transferred to the mass spectrometer through a 2 ml silica gel filled transfer tube equipped with an automated LN_2 pump. After collection, the O_2 is expanded into the sample bellow while the silica gel is heated to 95°C and the bellow is cycled from 90% to 25% six times over 30 minutes. Similar to the fluorination line operation, sample transfer to the mass spectrometer is automated to remove user dependencies. Machine analytical precision for all delta values are 0.002‰ or less. Precision (1σ) for analysis of silica is 0.08‰ for $\delta'^{18}O$ and 0.004‰ for $\Delta'^{17}O$ based on pooled variance of repeat analyses for silica samples analyzed to date. Equivalent precisions are attained for UWG-2 (n=7) which is used as a pinning standard (Valley et al., 1995).

Air O_2, used as a secondary standard for scaling purposes, is purified on a separate GC column filled with molecular sieve 5A held at -80°C (3.05 m × 1/8" OD; Agilent 7890B GC with thermal conductivity detector). The outflow of the GC separation is interfaced with the last

collection trap of the fluorination line allowing for sample transfer from the fluorination line to be identical to that for O_2 from silicates.

The scale compression correction follows the 'traditional linear' scheme of Schoenemann et al. (2013). Previously, we identified a scale compression in the raw isotope-ratio values from the mass spectrometer which is significant for triple oxygen isotope measurements and can be explained fully by a "pressure baseline" (PBL) effect (Yeung et al., 2018). The PBL effect results from scattering of ions/electrons within the flight tube of the mass spectrometer and is manifest as a nonzero baseline when the gas is entering the source. Provided that the beam intensity is fixed based on the major beam (*m/z*=32), the selected scheme approximates the theoretical correction of the PBL effect to well within analytical uncertainty (Yeung et al., 2018).

To compare our results directly with the temperature-dependent SiO_2-water fractionation calibration of Sharp et al. (2016), we normalize isotope ratios against the UWG-2 standard, which we assign a $\Delta'^{17}O$ value of -0.067‰ and a $\delta^{18}O$ value of 5.99‰ (Pack and Herwartz, 2014; Sharp et al., 2016). The measured $\Delta'^{17}O$ values for UWG-2 and San Carlos Olivine (SCO) differ by ~10 ppm on our setup. This result disagrees with that of (Pack and Herwartz, 2014), which showed only a 1 ppm difference between these standards. Considering that our SCO sample (SCO99-olv) may differ from that of other laboratories and that our measured compositions of SCO yield more variability than our measurements of UWG-2, we use UWG-2 as the primary standard. Further scaling of the triple-oxygen results is done by assigning a fixed difference in oxygen isotope compositions between Air-O_2 and UWG-2. The values used are $\Delta(\delta^{18}O)_{Air-UWG\text{-}2} = 17.4‰$, consistent with PBL corrected measurements from our laboratory and $\Delta(\Delta'^{17}O)_{Air-UWG\text{-}2} =$ -

0.421‰ which is consistent with previously published values corrected to VSMOW2-SLAP scaling (Yeung et al., 2018). This scheme yields inter-laboratory agreement in standard materials within 10 ppm for $\Delta'^{17}O$ (Yeung et al., 2018).

3. Results:

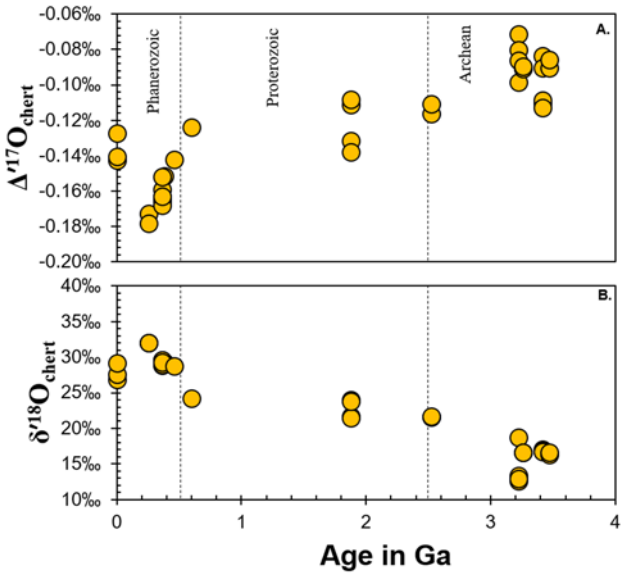

Fig. 1. *Oxygen triple-isotope composition of cherts through time.* ***a.*** *Measured $\Delta'^{17}O$ of cherts analyzed for this study. Point size is plotted to the precision of the measurement (0.004‰ 1σ).* ***b.*** *Measured $\delta'^{18}O(=ln[\delta^{18}O+1])$ of cherts analyzed for this study. Uncertainties for $\delta'^{18}O$ (0.08‰) are smaller than the point size.*

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207 **Table 1. Oxygen isotope composition of chert samples and standards.**

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Samples	Age (Ga)	$\delta'^{18}O$ (‰)	$\Delta'^{17}O$ (‰)	n
Monterey/Sisquoc Fm., California USA	0.005	32.435	-0.174	1
	0.005	32.267	-0.163	1
	0.005	27.184	-0.127	1
	0.005	28.011	-0.143	1
	0.005	29.602	-0.141	1
San Andres Limestone, New Mexico, USA	0.275	32.544	-0.176	2
Onate Fm., New Mexico, USA	0.39	29.726	-0.152	1
Caballos Novaculite, Texas, USA	0.3589	30.045	-0.164	1
	0.3589	29.840	-0.159	1
	0.3589	29.929	-0.166	1
	0.3589	29.366	-0.166	2
	0.3589	29.861	-0.158	2
Ellenberger Gp., Texas, USA	0.46	29.122	-0.142	1
Liuchapo Fm., China	0.6	24.536	-0.124	1
Gunflint Fm., Ontario, Canada	1.88	21.797	-0.110	2
	1.88	24.202	-0.135	2
Frisco Fm. , South Africa	2.521	21.826	-0.114	2
Moodies Gp., South Africa	3.22	13.391	-0.071	1
	3.22	12.889	-0.083	2
Mendon Fm., South Africa	3.258	18.880	-0.099	1
	3.258	16.746	-0.090	2
Kromberg Fm., South Africa Black chert (#1) of the BRC	3.416	16.988	-0.087	2
Kromberg Fm., South Africa Black chert (#2) of the BRC	3.416	17.165	-0.110	1
Kromberg Fm., South Africa White chert of the BRC	3.416	16.906	-0.111	2
Standards				
San Carlos Olivine		5.603	-0.057	11
UWG-2*		5.972	-0.067	7
Air O_2		23.222	-0.488	4

***assigned value discussed in text**

†Opal-CT

Precisions (1σ inter-sample reproducibility) for $\delta'^{18}O$ are 0.08‰. Precisions for $\Delta'^{17}O$ are 0.004‰ except for SCO yielding 0.012‰

The cherts show a trend of increasing $\delta'^{18}O$ and decreasing $\Delta'^{17}O$ values through time (Fig.1 and Table 1). The total range in $\Delta'^{17}O$ values is approximately 0.1‰, with an average decrease of 0.02‰ per billion years. Phanerozoic marine cherts are characterized by $\lambda = 0.5223 \pm 0.0014$ (1σ; the slope of a $\delta'^{17}O$ vs. $\delta'^{18}O$ cross-plot), and Precambrian cherts by $\lambda = 0.5263 \pm 0.0006$. These λ values suggest that different processes and/or reservoirs govern oxygen triple-isotope variations in Phanerozoic and Precambrian cherts. Where repeat analyses were done (majority of samples; see supplemental) different analyses of the same band or region of the cherts yields nearly equivalent results, indicating homogeneity of oxygen isotopes in these samples at spatial scales greater than our sampling scale (~1 mm^3). Our choice to use the pooled variance of these analyses for our analytical uncertainty means that any homogeneity at this scale is factored into our uncertainty (±0.004‰ for $\Delta'^{17}O$ and ±0.08‰ for $\delta'^{18}O$).

4. Discussion

4.1 Phanerozoic cherts

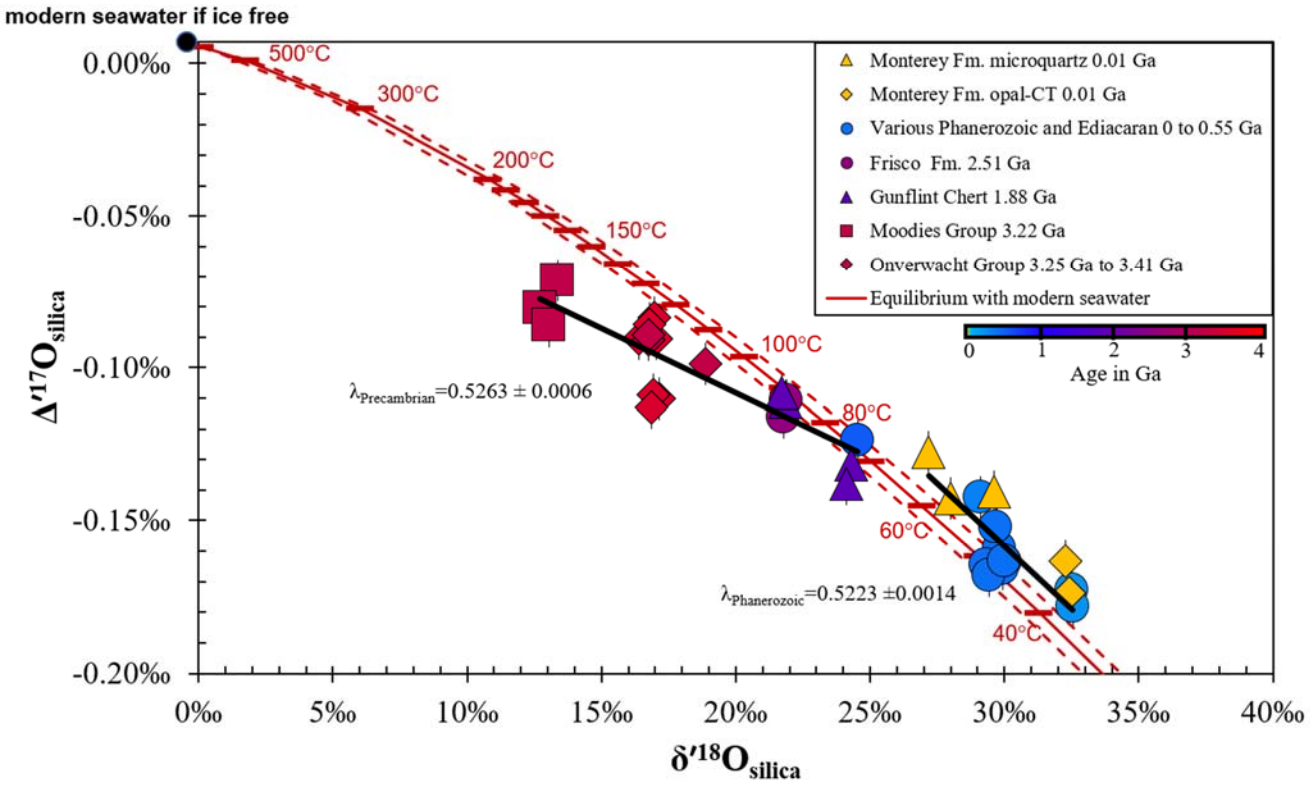


Fig. 2. $\delta'^{18}O$ vs. $\Delta'^{17}O$ of cherts and two Neogene Opal-CT samples. Uncertainties are the same as in Fig. 1. The red curve is the range of silica triple-oxygen isotope compositions compatible with formation in the modern ice-free ocean [$\delta^{18}O$= -1‰, $\Delta'^{17}O$ = 0.0075‰ calculated using data in Sharp et al. (2018)] based on the empirical silica-water fractionation estimate of Sharp et al.(Sharp et al., 2016) with slight modification from Wostbrock et al. (2018). Dotted lines around the fractionation curve correspond to compositions of water ±1‰ from a modern ice-free ocean.

The oxygen-isotope compositions of chert and opal-CT in the Miocene Monterey Formation (0.01 Ga) are consistent with growth from a water that has a composition offset from a modern (ice-free) ocean by either +1.5‰ in $\delta^{18}O$, +0.008‰ in $\Delta'^{17}O$, or some intermediate composition within those bounds (see Fig. 2). This difference could be explained by slight

analytical differences between our calibration and that used for the silica-water fractionation curve (Sharp et al., 2016; Wostbrock et al., 2018). Therefore, the growth waters for these cherts are isotopically indistinguishable from ice-free modern seawater (hereafter "isotopically modern" seawater), although a small porewater oxygen-isotope change during chert diagenesis cannot be ruled out. The Miocene opal and chert compositions are plausibly explained by an open seawater-porewater system that recrystallizes silica at various temperatures during burial. This interpretation is consistent with previous work on silica (Murata et al., 1977) and carbonates (Loyd et al., 2012) in diagenetic settings that showed little evidence for significant porewater $\delta^{18}O$ evolution. We thus interpret the λ value of 0.5223 from the Miocene cherts to result from chert recrystallization in pore waters of constant isotopic composition over a range of temperatures. For this environment, the diagenetic fluid appears to be a proxy for the isotopic composition of coeval seawater.

Similar to the Miocene cherts, the oxygen-isotope compositions of older Phanerozoic cherts are consistent with growth from a fluid resembling modern seawater in its oxygen-isotope composition. Implied growth temperatures based on $\delta'^{18}O$ in such waters are between approximately 35°C and 60°C, with a modal temperature of 47°C and no clear correlation between temperature and age. These conditions, and the range in $\delta'^{18}O$ and $\Delta'^{17}O$ values, are consistent with early diagenetic transformation of low-detritus Opal-A to Opal-CT or microquartz beneath the seafloor (Keller and Isaacs, 1985). Furthermore, samples identified as opal-CT from the Monterey Formation (Table S3) yield formation temperatures near 35°C, which are consistent with the expectation of lower diagenetic temperatures associated with opal-CT formation (Keller and Isaacs, 1985). This result suggests (1) the isotopic equivalence of seawater and pore fluids in the environment of chert diagenesis holds through the Phanerozoic

and (2) the oxygen isotope composition of seawater has remained roughly constant since at least the Ordovician. This latter interpretation corroborates recent carbonate clumped-isotope results, which suggest a seawater $\delta^{18}O$ value bound within ~2‰ since the Cambrian (Coogan et al., 2019; Cummins et al., 2014; Henkes et al., 2018; Ryb and Eiler, 2018).

Previously Phanerozoic and Archean cherts were measured by Levin et al. (2014) who reported $\Delta'^{17}O$ values relative to UWG-2 measured in their laboratory. Normalizing their chert results to the UWG-2 composition used here yields mean $\Delta'^{17}O$ values that are lower than ours by 0.1‰. The reason for this difference cannot be determined with the information provided in Levin et al. (2014), although the larger uncertainties in $\Delta'^{17}O$ standards (e.g., 1σ = 0.052‰ for UWG-2 and 0.035‰ for NBS-28) suggest that at least some part of the disagreement can be explained by random error. Potential unquantified triple-oxygen scale compression is difficult to diagnose in that study given the small $\delta'^{18}O$ range (4‰) of the standards used. We note that our reported Phanerozoic chert compositions more closely match marine quartz compositions with approximately the same $\delta^{18}O$ reported in Sharp et al. (2018).

4.2 Precambrian Cherts

Unlike for the Phanerozoic cherts, the oxygen-isotope compositions of the Latest Archean and Proterozoic cherts require diagenetic recrystallization at higher temperatures (70-90°C) and/or in isotopically different waters from those of the Phanerozoic. Paleoarchean cherts cannot have formed in isotopically modern seawater, invalidating an early hypothesis that they had grown at elevated temperatures from such fluids (Knauth and Lowe, 2003). Potential explanations for triple-oxygen compositions of Precambrian cherts involve scenarios in which (*i*) the initial growth fluids had a different isotopic composition, (*ii*) the cherts are internally mixed,

i.e., representing multiple generations of silica precipitation that occurred under different conditions, or (*iii*) the cherts have been altered after initial deposition. Below, we evaluate these potential explanations for the isotopic composition of Precambrian cherts, with a focus on those of the Paleoarchean.

4.2.1 Scenarios 1 and 2: Early diagenesis in low-$\delta'^{18}O$, high-$\Delta'^{17}O$ fluids

If the early diagenesis of Phanerozoic cherts is a satisfactory model, i.e., recrystallization occurred between 35˚C and 60˚C, then one can estimate the fluid composition required to precipitate Precambrian cherts in that environment. Using this approach, the oxygen triple-isotope composition of Onverwacht Group cherts ($\delta'^{18}O$ = 17.165‰, $\Delta'^{17}O$ = -0.090‰ on average) imply a diagenetic fluid of $\delta'^{18}O = {}^{-}16.4$‰ to ${}^{-}10.7$‰ and $\Delta'^{17}O$ = 0.103‰ to 0.057‰ for the Paleoarchaean. Under this interpretation, younger cherts are compatible with growth in fluids that were isotopically closer to modern seawater, but those fluids still must have lower $\delta'^{18}O$ and higher $\Delta'^{17}O$ values. The origins of these low-$\delta'^{18}O$, high-$\Delta'^{17}O$ fluids is enigmatic; we explore the possibility that lighter diagenetic fluids represent (1) meteoric waters and (2) coeval seawater.

The Precambrian cherts can be described by a singular trend different from the Phanerozoic cherts, with a λ value of 0.5263. This λ value is indistinguishable from that characterizing meteoric waters with $\delta^{18}O$ > -20‰ [$\lambda = 0.5265 \pm 0.0003$; (Sharp et al., 2018)]. A possible explanation for the compositions of Precambrian cherts is thus subsurface intrusion of meteoric waters into the early diagenetic environment where they recrystallized. The isotopically lightest cherts presented here would require nearly pure meteoric waters with low $\delta'^{18}O$ values ≤ -11‰ if water-to-rock ratios are high. Explaining the temporal trend in triple-oxygen

composition using this mechanism requires that meteoric water be a ubiquitous component of Precambrian chert growth fluids, but insignificant for their Phanerozoic equivalents. If this interpretation is correct, then the need for this dichotomy in chert formation conditions is further evidenced by larger compilations of chert $^{18}O/^{16}O$ ratios (Bindeman et al., 2016). Whether a secular change in chert diagenesis of this nature occurred over Earth history is not known.

However, it is clear from studies of the Paleoarchean cherts of the Onverwacht Group (3.41 Ga to 3.25 Ga; plotted as diamonds in Figure 2) and the Buck Reef chert in particular (BRC; 3.41 Ga), that at least some Paleoarchean cherts underwent early diagenetic recrystallization in an environment similar to that for the Phanerozoic cherts (Knauth and Lowe, 2003). The lines of supporting evidence include: the range of $\delta'^{18}O$ values matching the ~7‰ range of Phanerozoic cherts (despite lower mean values), the apparent early silicification and brecciation of "white cherts" of the BRC and Mendon Formation, and silicification prior to the compaction of carbonaceous particles and relicts of opal-CT lepispheres (Hren et al., 2009; Knauth and Lowe, 2003; Stefurak et al., 2015; Tice and Lowe, 2006; Trower and Lowe, 2016). Furthermore, the chert shows no evidence for exogenous inputs from meteoric waters based on δD-$\delta^{18}O$ trends, which are more consistent with early diagenesis at temperatures below 55°C (Hren et al., 2009). The recrystallization fluid for the samples in that study were thus interpreted to be coeval diagenetic fluids.

The samples of BRC analyzed this study were sampled from one of two sections utilized in the Hren et al. (2009) study, so their geologic context is presumed to apply. If the composition of the BRC "white" chert is used to solve for the porewater composition—because they are of higher purity (Table S2), show no textural evidence of secondary silica (Figure S4), and are believed to have silicified first—then the diagenetic fluid would have $\delta'^{18}O$ = –16.6‰ to –11.0‰

and $\Delta'^{17}O$ = 0.092‰ to 0.044‰, still different from isotopically modern seawater. Note that the white chert from the BRC analyzed here has a lower $\delta'^{18}O$ (16.9‰) than equivalent samples from the previous study, with a composition closer to the black cherts in the unit. It may indicate that these particular samples of white chert recrystallized at roughly the same temperature as the surrounding black chert. In general, the measured cherts from this age have $\delta'^{18}O$ values at the low end of those previously measured (Hren et al., 2009; Knauth and Lowe, 2003). Cherts with these compositions have been previously interpreted as representing the highest-temperature diagenetic phase.

Interestingly, the two 1.88 Ga Gunflint cherts measured here define a triple-oxygen trend roughly parallel to the trend observed for the Phanerozoic cherts. This parallel trend may imply a similar diagenetic environment in a fluid of intermediate composition (i.e., $\delta^{18}O \sim -4‰$), but with the limited data currently available it is not yet possible to determine if this trend is coincidental. Parallel, triple-isotope trends resembling the Phanerozoic trend within a sequence would be evidence that the chert oxygen-isotope compositions reflect an early diagenetic environment similar to Phanerozoic cherts.

4.2.2 Scenario 3: Mixtures of high- and low-temperature phases

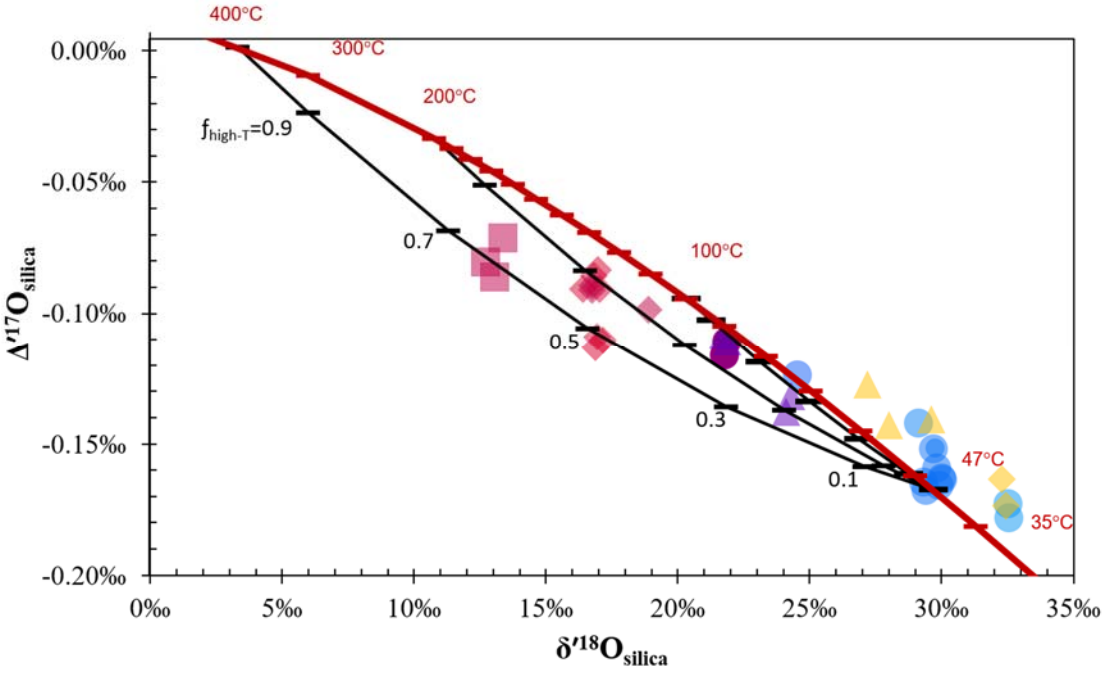


Fig. 3. High and low temperature chert mixture models. The red curve is the range of silica triple-oxygen isotope compositions compatible with formation in modern ice-free seawater). Black lines are two-endmember mixing curves between a higher temperature chert endmember and a lower temperature endmember that were crystallized in porewaters of the same isotope composition. The chert triple oxygen isotope compositions are plotted for comparison.

An alternative explanation for the triple-isotope compositions of Precambrian cherts is for them to be mixtures of silica crystallized at different temperatures. Figure 3 shows two-endmember mixing curves for high- and low-temperature silica mixtures assuming the pore water composition in the two environments is equal to isotopically modern seawater. All the Precambrian cherts can be explained as mixtures of silica crystallized in early diagenetic environments and silica

crystallized between 100˚C and 400˚C. Generally, the Archaean cherts require a higher-temperature silica mixing endmember than the Proterozoic cherts. The secular trend in oxygen-isotope compositions would then reflect a cooling of the high-temperature endmember over Earth history.

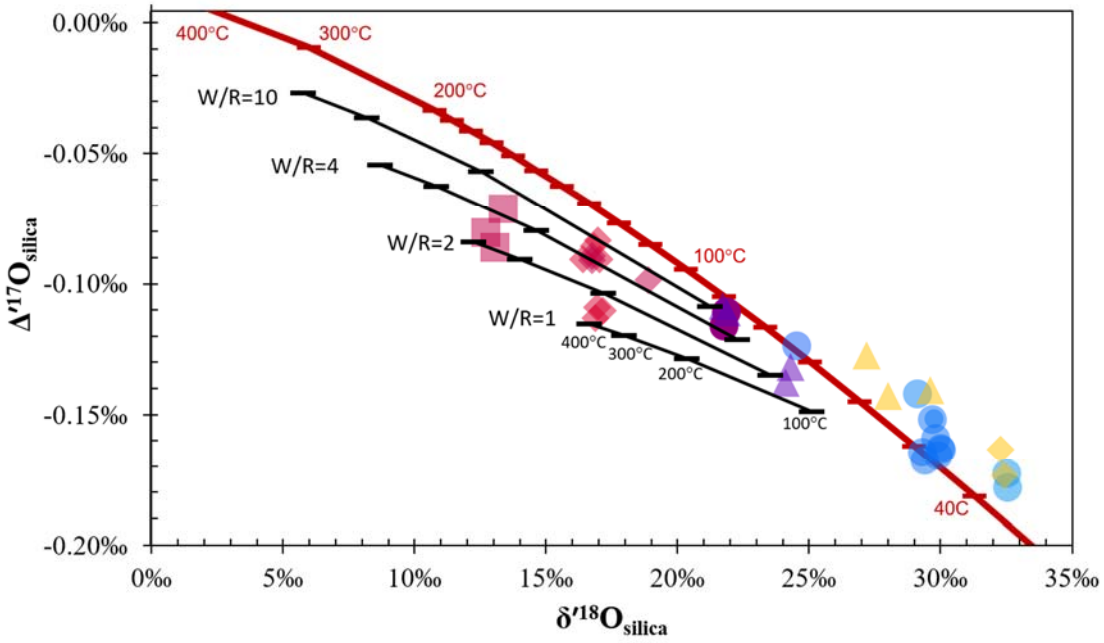
If the cherts analyzed here are mixtures of high- and low-temperature silica, the heterogeneity would need to manifest at a scale <1 mm^3, perhaps at the scale of microquartz grains (10^{-5} mm^3). Microanalytical techniques may be able to test this hypothesis. A broad distribution in $\delta^{18}O$ has been observed in some Precambrian cherts, particularly those of the 1.88 Ga Gunflint Formation, examples of which were also analyzed here (triangles in Figures 2 and 3). Previous work indicated an isotopic heterogeneity of ~12‰ at a 2 μm scale in the Gunflint chert, which was taken as evidence for the presence of a ~130°C hydrothermal silica mixing endmember (Marin et al., 2010). Mixing between a high-temperature silica endmember at 120°C (~40%) and a low-temperature silica endmember at 47˚C (~60%), both formed in isotopically modern seawater, can explain the triple-oxygen composition of our Gunflint chert samples. However, this particular mixture is not unique; there exists a continuum of scenarios for two-endmember (high- and low-temperature silica) mixtures that can explain these samples if the oxygen-isotope composition of the growth fluid is allowed to vary. For example, a difference in $\delta^{18}O$ of 12‰ can also be attained if the two end members formed in the same water at temperatures of ~20°C and ~70°C, as is reasonable for the early diagenetic environment. This particular scenario is compatible with water compositions of $\delta^{18}O$ < -4‰ using the bulk oxygen isotope compositions of Gunflint chert measured here.

4.2.3 Scenario 4: Late, closed-system recrystallization of silica

Finally, we investigate closed-system recrystallization as a possible explanation for the oxygen-isotope trends in Precambrian cherts. This mechanism was previously considered by Sengupta and Pack (2018), although our formulation differs slightly in implementation. The equations for the closed-system water-rock interactions are given by:

$$\left(\frac{W}{R}\right) R_{w,i} + R_{r,i} = R_{w,f}\left[\alpha + \left(\frac{W}{R}\right)\right] \quad \text{Eq.1}$$

where R is the ratio of the heavy isotope to the light isotope, i.e., $^{17}O/^{16}O$ or $^{18}O/^{16}O$, α is the temperature dependent fractionation factor for the rock (SiO_2) relative to water, the subscripts w and r indicate the parameters for water and rock, respectively, and the subscripts i and f indicate initial and final compositions, respectively. W and R are the amounts of oxygen held in water and the silica phase, respectively.



393

394 *Fig. 4. Closed-system chert recrystallization model results. The red curve is the range of*
395 *silica triple-oxygen isotope compositions compatible with formation in modern ice-free*
396 *seawater. Black lines give results for closed-system recrystallization at a range of water-rock*
397 *ratios (W/R) and temperatures. The chert triple oxygen isotope compositions are plotted for*
398 *comparison.*

399

400 We find that for cherts initially formed at 47˚C (in modern seawater) and diagenetic fluids
401 resembling modern seawater, the secular trend of Precambrian cherts can be explained by closed-
402 system recrystallization for $1 \leq W/R \leq 10$ (see Fig. 4); however, the temperature of alteration must
403 undergo a secular decrease through Earth' history. For example, using W/R = 4, the Onverwacht
404 cherts (~3.4 Ga) would be best explained with a closed-system alteration temperature of 175°C,
405 while the cherts from the Frisco Formation (2.51 Ga) require a temperature of 110°C. If the

406 diagenetic fluid were meteoric instead, higher water-to-rock ratios are needed to explain the chert
407 compositions, but secular cooling of those fluids is still required.

408 The need for high water-to-rock ratios argues against the water-rock system being closed
409 at the grain-scale; for example, if the initial phase consisted of silica granules, as might be implied
410 by the presence of ripples and cross bedding in the Onverwacht cherts (Tice and Lowe, 2006), then
411 using a typical porosity of 35%, the bulk W/R ratio is calculated to be ~0.34. Instead, higher water-
412 to-rock ratios require that the closed system is at the formation scale, perhaps consisting of a
413 permeable, but unreactive rock that is spatially separated from the samples being analyzed. To
414 achieve a W/R ratio of 1 using a nominal water-filled porosity of 0.35 would require that 66% of
415 the rock in the system is unreactive. Higher water-to-rock ratios would require more of the system
416 to be unreactive, for instance 91% unreactive to reach a W/R of 4. Such a scenario could result
417 from exchange occurring fastest at the base of a sediment column, where temperatures are highest,
418 but at a rate slower than the circulation rate of the fluid within the system. In that case, one might
419 expect distinct closed-system recrystallization trends down-section for different formations in
420 which permeabilities, porosities, burial rates, and thermal histories differ. In effect, the diagenetic
421 fluids of these formations would all be different, yielding disparate trajectories in triple-isotope
422 space. More exhaustive compilations of chert triple-isotope data, once available, will be able to
423 test this hypothesis.

424

425

426 **4.3. Potential implications and relationship to other proxies for ancient temperatures**

427 We will first explore the implications if the BRC samples crystallized in Paleoarchaean
428 diagenetic fluids. Here, we use the interpretation that the BRC represents a diagenetic sequence

similar to that of Phanerozoic cherts (Hren et al., 2009; Knauth and Lowe, 2003). $\delta'^{18}O$ values as high as 22‰ have been reported in the BRC and interpreted to reflect the lowest-temperature diagenetic phase in the unit (Knauth and Lowe, 2003). Thus, using $\delta'^{18}O = {}^{-}11‰$ for the diagenetic fluid and $\delta'^{18}O$ = 22‰ for the BRC yields a minimum diagenetic temperature of 37°C. This temperature also serves as an upper limit on seafloor temperatures for this locality during the Paleoarchean. The relatively low temperature is in agreement with the temperature limit (<55°C) inferred from δD-$\delta'^{18}O$ pairings (Hren et al., 2009) and the presence of possible diamictites and gypsum pseudomorphs in lower units of the Onverwacht (de Wit and Furnes, 2016). Moreover, it is feasible based on recent climate-model predictions (Charnay et al., 2017; Krissansen-Totton et al., 2018) We note that a minimum diagenetic temperature of 37°C aligns with the lowest temperature of chert diagenesis we observe in Phanerozoic cherts (~35°C), making this estimate and interpretation self-consistent.

The cherts of the Onverwacht Group have been interpreted as marine due to the large lateral extent of the chert units, the need for large amounts of silica to account for hundreds of meters of silicified rocks and the presence of evaporites (indicating a saline environment). Thus, interpreting the chert growth waters as the coeval diagenetic fluid leads naturally to the interpretation that seawater in the Archean was significantly isotopically lighter. If the diagenetic fluid approximates coeval seawater for the Precambrian samples—as is case for Phanerozoic cherts—the triple-isotope data suggest that seawater became progressively more ^{18}O-enriched over geologic time (Fig. S1). Any feasible mechanisms for accomplishing a lower $\delta'^{18}O$ for Paleoarchean seawater require more intense low temperature water-rock interactions and/or less intense high temperature water-rock interactions earlier in Earth's history (Jaffrés et al., 2007; Kasting et al., 2006; Pack

and Herwartz, 2014; Wallmann, 2004). Modeling studies suggest that a seawater $\delta'^{18}O$ value of -11‰ can only be achieved by dramatically reducing the proportion of water-rock interactions occurring at high temperatures (Jaffrés et al., 2007; Kasting et al., 2006). Such a scenario could be realized if submarine magmatic centers were shallower in the Archean, perhaps associated with higher mid-ocean ridge crests or more extensive volcanic plateaus (Kamber, 2010; Kasting et al., 2006; Lambert, 1980). Alternatively, a more sluggish tectonic regime in the Archean (Tang et al., 2016), characterized by a reduced area of magmatic activity, could lead to a reduction in high-temperature water-rock chemistry.

The Archaean seawater composition implied by the early-diagenesis interpretation of Archean cherts can be compared with estimates obtained from other proxies. The $\delta'^{18}O$ values in iron-associated phosphate and kerogen-bound oxygen (Blake et al., 2010; Tartèse et al., 2017) may first appear to be in disagreement, but the reported uncertainties of those approaches allow them to be compatible with local surface water having $\delta'^{18}O \geq {}^{-}10$‰ (Chang and Blake, 2015; Tartèse et al., 2017). Thus, the composition of seawater is not further constrained by these proxies.

Sengupta and Pack (2018) recently constructed an empirically constrained seawater triple-isotope model based on the model of Muehlenbachs (1998). The mass-balance model yields a λ value for seawater evolution of 0.51, which is incompatible with the λ value of 0.526 from Precambrian cherts in this study if they indeed formed in a fluid resembling Paleoarchaean seawater. Reconciling the geological constraint indicating that the cherts of the Onverwacht Group in general, and the BRC specifically, represent a diagenetic environment with this study requires the diagenetic fluids be isotopically depleted relative to coeval seawater. Further constraints can be provided with additional chert triple oxygen isotope compositions.

The other scenarios we consider, i.e. the involvement of meteoric water, late closed system recrystallization and mixtures between silica formed at high temperature and low temperatures, imply other secular Earth system trends. In the case of the involvement of meteoric water, a trend in paleolatitude or paleoaltitude of the source waters would be needed to explain the chert compositions. Another possible explanation is that of progressive alteration in meteoric waters over the cherts long history, but this has been argued against in the past (Knauth and Lowe, 2003). For the other potential explanations, the common trend is the need to invoke a secular change in the temperature of later alteration. Assuming burial rates are constant, as they would be governed by surface processes, the simplest explanation is a secular change in the geothermal gradient in the environment of chert diagenesis. A steeper geothermal gradient in the Archean would bring the depth with sufficient temperature closer to the surface possibly allowing these cherts to reach the needed temperatures prior to the loss of their porosity. This may be explained by higher heat production for the young Earth. Although studies estimating Archean geothermal gradients largely focus on the gradient at greater depth, geothermal gradients on Archean cratons are thought to be similar to the modern (Ballard and Pollack, 1988; Lenardic, 1998). It is unclear if near-surface geothermal gradients should be sufficiently higher in Earth's deep past.

Regardless of the interpretation, the presence of a long-term triple-oxygen isotope trend in Precambrian cherts implies a secular evolution of some boundary condition relevant to chert diagenesis affecting the isotopic composition of the fluid. Moreover, this evolution appears to have ceased by the beginning of the Phanerozoic, or has not yet significantly affected Phanerozoic cherts. Examples of these boundary conditions are the composition of intruding meteoric waters (e.g. driven by steadily decreasing paleolatitude for the sections), the global-mean temperature of seawater-rock interactions (i.e. resulting in a change in seawater $\delta'^{18}O$) or the temperature of

hypothetical high-temperature alterations (i.e. secular change in the geotherm). These potential explanations are not exclusive and any combination of them would be consistent with chert oxygen isotope results. We note that shales, carbonates, and cherts share similar oxygen-isotope trends through geologic time (Bindeman et al., 2016); our chert $\Delta'^{17}O$ record resembles that recently reported for shale, in particular [(Bindeman et al., 2018); see also Fig. S1]. A parsimonious explanation for the overall trend is the $\delta'^{18}O$ value of seawater evolved from -11‰ or lower during the Paleoarchean to a modern composition by the Ordovician. However, conflicting geochemical and modeling evidence in the literature precludes a definitive interpretation at this time (Blake et al., 2010; Sengupta and Pack, 2018; Tartèse et al., 2017).

5.1 Conclusions:

The triple-oxygen isotope composition of marine cherts from 3.5 billion years of Earth's history indicate a switch in some aspect of the factors leading to the oxygen isotope composition of chert occurring at some time prior to the Ordovician. The oxygen isotope composition of Phanerozoic cherts reflect recrystallization over a range of early diagenetic temperatures (35°C-60°C) in a water indistinguishable from that of the modern ocean ($\delta^{18}O = 0 \pm 2$‰). Importantly, the additional constraint provided by ^{17}O shows that low $\delta^{18}O$ values of Archean cherts are incompatible with a hot (>70°C) surface and an isotopically modern oceans in the Archaean. Geological and geochemical constraints from the literature implying an early diagenetic origin for a subset of the measured Archean cherts, when combined with the data presented here, suggests that at 3.45 Ga diagenetic fluids had a $\delta^{18}O$ value of < -11‰, with surface temperatures <34°C. While this result may be used to indicate a secular evolution or seawater $\delta'^{18}O$, alternate

519 feasible explanations for the chert compositions remain which do not require a change in
520 seawater $\delta'^{18}O$.
521
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530 Hayles and Hehe Jiang. All authors contributed to interpretations.
531

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Data and materials availability: All data is available in the main text or the supplementary materials.