

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

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11 **Keywords:** Archean, chert, triple-oxygen-isotopes, marine silica

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13 **Highlights:**

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

19
20 **Abstract:** The $^{18}\text{O}/^{16}\text{O}$ ratios of ancient marine minerals show a puzzling increase over geologic
21 time. Long-term changes in temperature, seawater $^{18}\text{O}/^{16}\text{O}$ ratios, and post-depositional
22 overprinting can all explain this trend, but few tracers can distinguish between these scenarios.
23 Here, we report high-precision $^{18}\text{O}/^{16}\text{O}$ and $^{17}\text{O}/^{16}\text{O}$ ratios of cherts through 3.4 Ga of Earth's
24 history. We find that Phanerozoic cherts are consistent with having formed in porewaters that are
25 isotopically indistinguishable from modern (ice-free) seawater. In contrast, Precambrian cherts
26 require either formation in waters isotopically distinct from Phanerozoic seawater, or a different
27 mode of formation. If the early diagenetic formation pathway of Precambrian cherts resembles that
28 of Phanerozoic cherts, and the Precambrian cherts are unaltered, then the results would imply that
29 the oxygen-isotope composition of seawater has evolved on billion-year timescales before
30 reaching its present composition by the Ordovician. Under this interpretation it is estimated that
31 seawater had $\delta^{18}\text{O} < -11\text{‰}$ at 3.41 Ga, with surface temperatures $< 34^\circ\text{C}$. Although this scenario
32 provides the simplest explanation for the observed $^{18}\text{O}/^{16}\text{O}$ trend of marine minerals, other
33 scenarios which do not require a secular change in seawater $^{18}\text{O}/^{16}\text{O}$ cannot be ruled out.
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36 **1.1 Introduction:**

37 The oxygen isotope composition of seawater is buffered over geologic time by a balance
38 of high- and low-temperature interactions with the silicate Earth (Gregory and Taylor, 1981;
39 Muehlenbachs, 1998; Muehlenbachs and Clayton, 1976). These interactions have likely confined
40 the $^{18}\text{O}/^{16}\text{O}$ ratio in seawater to within a small range over the Phanerozoic (i.e. linearized notation:
41 $\delta^{18}\text{O} = \ln[\delta^{18}\text{O}+1] = 0 \pm 2\%$ relative to VSMOW) (Coogan et al., 2019; Cummins et al., 2014;
42 Henkes et al., 2018). High-temperature interactions, such as those at seafloor hydrothermal
43 systems, tend to increase seawater $\delta^{18}\text{O}$ values, while low-temperature interactions with oceanic
44 and continental crust tend to lower seawater $\delta^{18}\text{O}$ values. Yet, details of how this seawater
45 buffering system operated for early Earth are unknown. The evolution of seawater $\delta^{18}\text{O}$ may offer
46 clues to the evolution of the solid Earth over geologic time (Jaffrés et al., 2007; Kasting et al.,
47 2006). Changing subaerial exposure of mid-ocean ridges, penetration depths of seafloor
48 hydrothermal circulations, effective seafloor spreading rates, and the spatial extent of volcanic
49 plateaus can all affect seawater $\delta^{18}\text{O}$ values by altering the proportions of high- and low-
50 temperature water-rock interactions at the global scale (Jaffrés et al., 2007; Kamber, 2010; Kasting
51 et al., 2006).

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

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

69 We hypothesize that $^{18}\text{O}/^{16}\text{O}$ and $^{17}\text{O}/^{16}\text{O}$ isotope ratios of cherts—i.e., their triple oxygen-
70 isotope composition—can constrain the $\delta^{18}\text{O}$ of ancient porewaters. Ultra-high-precision oxygen
71 triple-isotope measurements (quantified as $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.5305 \times \delta^{18}\text{O}$) allow one to probe the
72 $\delta^{18}\text{O}$ - $\Delta^{17}\text{O}$ relationships between phases, which are bounded by physical-chemical constraints
73 (Cao and Liu, 2011; Hayles et al., 2018; Hayles et al., 2017). For a given source-water $\delta^{18}\text{O}$ and
74 $\Delta^{17}\text{O}$ value, only a bounded range of chert compositions are possible at equilibrium (Hayles et al.,
75 2018; Sharp et al., 2016; Wostbrock et al., 2018). Similarly, the oxygen triple-isotope composition
76 of a given chert is only consistent with a narrow set of growth waters. The low permeability and
77 low oxygen diffusivity in microquartz cherts render them an ideal phase to analyze these variations
78 because they are resistant to alteration once the crystalline quartz phase has formed (Knauth,
79 1994): experimental measurements of oxygen diffusion rates in grain boundaries of natural chert

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

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

88 To date, triple-oxygen compositions of only one set of Precambrian (2.5 Ga) and
89 Phanerozoic cherts has been published (Levin et al., 2014). Their compositions show no coherent
90 pattern, but are generally lower in $\Delta^{17}\text{O}$ than expected for equilibrium with seawater at a given
91 $\delta^{18}\text{O}$ value. Closed-system hydrothermal alteration was suggested as a potential driver of triple-
92 oxygen variability in the rock record, although one Phanerozoic chert (~65 Ma Stevns Klint chert)
93 was found to be unaltered (Sengupta and Pack, 2018). Given the sparsity of chert triple-oxygen
94 data, it is not known if the secular evolution in $\delta^{18}\text{O}$ values is also present in $\Delta^{17}\text{O}$ values. If the
95 secular evolution in chert $\delta^{18}\text{O}$ values is mirrored in their $\Delta^{17}\text{O}$ values, chert oxygen-isotope
96 compositions may be diagnostic of changing Earth-system processes through Earth history.

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

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

105 **2. Materials and Methods:**

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107 **2.1 Materials**

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109 Chert samples for this study were taken from units covering 3.4 billion years of Earth's
110 history from three modern day continents. Samples for this study were taken from the
111 Monterey/Sisquoc Formation (Miocene) of California, San Andres Limestone (Permian) and
112 Onate formation (Devonian) of New Mexico, Caballos Novaculite (Devonian) and Ellenberger
113 Group (Ordovician) of Texas, Liuchapo Formation (Ediacaran) of China, Gunflint Formation
114 (1.880 Ga) in Ontario and the Frisco Formation (2.521 Ga), Moodies Group (3.22 Ga), Mendon
115 Formation (3.258 Ga) and Kromberg Formation (3.41 Ga) of South Africa. Specific localities,
116 references for the samples, GPS coordinates, where known, and some further sample information
117 can be found in Table S1 in the supplemental. Samples are selected based on purity because the
118 analytical technique for oxygen isotopes cannot discriminate between the silica component of
119 chert and detrital components. All samples have been analyzed by LA-ICPMS to verify purity is
120 greater than 98% SiO₂, but the results for only a subset of these samples are presented in the
121 supplemental with the remainder to be presented at a later date.

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123

124 **2.2 Methods**

125 Oxygen isotope analyses were conducted at Rice University using techniques previously
126 described (Yeung et al., 2018). Prior to oxygen isotope analysis, 2-3 mg chert samples and
127 silicate standards are loaded onto a sample plate made of 316L steel. The sample plate is then
128 placed into a cell in the laser fluorination line equipped with a ThF₄ coated ZnSe window. The
129 cell is evacuated to high vacuum using a turbo pump and an infrared lamp is used to heat the
130 sample plate through the window. The heating and pumping are continued until the pressure
131 measured at the pump reads 10^{-6} mbar. When all samples are individual grains, this heating step
132 typically lasts for 3 days, but can take up to a week if hydrous (e.g. opal) or powdered samples
133 are loaded. At the end of this step, the cell containing the samples is filled with ~30mbar of pure
134 F₂ gas generated by heating of a potassium fluoronickelate salt (Asprey, 1976). The purity of the
135 F₂ gas, and in particular the lack of O₂, is verified using periodic F₂-only blank tests mimicking
136 the fluorination procedure but lacking the laser heating step. The samples and standards are
137 exposed to the fluorine gas atmosphere at room temperature for two days. This prefluorination
138 step is done to remove any further traces of moisture from the samples but in no instance was an
139 O₂ yield from this step observed.

140 Oxygen from silica samples and silicate standards are converted to O₂ gas by reaction with
141 a two-fold excess of purified F₂ gas. Typical operating pressure of F₂ is 60 mbar. Heat for the
142 reaction is provided by a 10.6 μm CO₂ laser (Synrad 48-2; 25W). Reaction temperatures are
143 unknown, but the majority of the reaction proceeds above the melting temperature of the silicates
144 and yields are complete. For all chert samples, no residues remained in the cell after fluorination
145 indicating the samples were composed of pure silica as most common metal fluorides are solids
146 under the reaction conditions. The purity of the silica was confirmed for the samples which LA-
147 ICPMS and electron microprobe analyses were performed (see Supplemental Information). The

148 resulting gas mixture of F₂, O₂, SiF₄ and trace impurities (e.g. CF₄, NF₃) is first purified
149 cryogenically at -196°C to remove SiF₄ and any other condensable reaction products (e.g. trace
150 CF₄). This is followed by reaction of the F₂ with KBr held at 215°C and condensation of the
151 products at -196°C. The resulting roughly purified O₂ is collected onto a U-trap filled with silica
152 gel and forwarded through a 3.05 m × 1/8" OD gas chromatography (GC) column filled with
153 molecular sieve 5A (80/100 mesh) in a 20 mL/min flow of He carrier gas to remove any trace
154 NF₃. Beginning at ~2 minutes after introduction and ending 10 minutes after introduction, the
155 purified O₂ is recollected in a second silica gel filled U-trap. All processes after the fluorination
156 reaction are automated in order to reduce user-derived variability therein.

157 The resulting purified O₂ is analyzed for triple oxygen isotope composition on a Nu
158 Instruments *Perspective IS* mass spectrometer (PS001) equipped with a dual inlet and directly
159 connected to the fluorination line. Oxygen gas is transferred to the mass spectrometer through a 2
160 ml silica gel filled transfer tube equipped with an automated LN₂ pump. After collection, the O₂
161 is expanded into the sample bellow while the silica gel is heated to 95°C and the bellow is cycled
162 from 90% to 25% six times over 30 minutes. Similar to the fluorination line operation, sample
163 transfer to the mass spectrometer is automated to remove user dependencies. Machine analytical
164 precision for all delta values are 0.002‰ or less. Precision (1σ) for analysis of silica is 0.08‰ for
165 δ¹⁸O and 0.004‰ for Δ¹⁷O based on pooled variance of repeat analyses for silica samples
166 analyzed to date. Equivalent precisions are attained for UWG-2 (n=7) which is used as a pinning
167 standard (Valley et al., 1995).

168 Air O₂, used as a secondary standard for scaling purposes, is purified on a separate GC
169 column filled with molecular sieve 5A held at -80°C (3.05 m × 1/8" OD; Agilent 7890B GC with
170 thermal conductivity detector). The outflow of the GC separation is interfaced with the last

171 collection trap of the fluorination line allowing for sample transfer from the fluorination line to
172 be identical to that for O₂ from silicates.

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

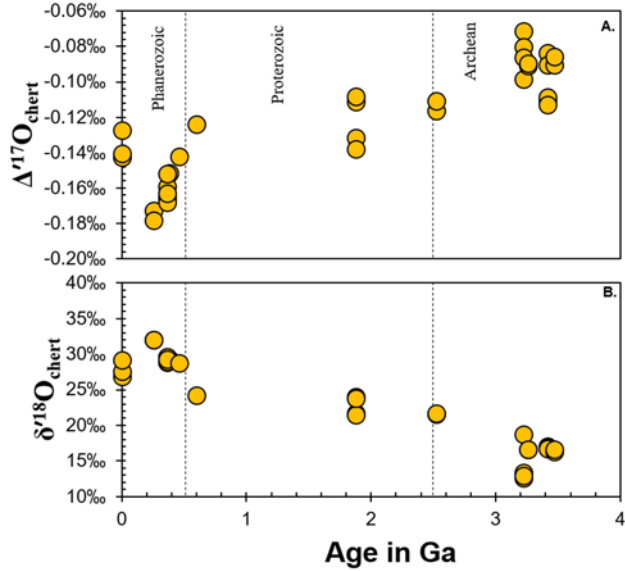
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183 To compare our results directly with the temperature-dependent SiO₂-water fractionation
184 calibration of Sharp et al. (2016), we normalize isotope ratios against the UWG-2 standard, which
185 we assign a $\Delta^{17}\text{O}$ value of -0.067‰ and a $\delta^{18}\text{O}$ value of 5.99‰ (Pack and Herwartz, 2014; Sharp
186 et al., 2016). The measured $\Delta^{17}\text{O}$ values for UWG-2 and San Carlos Olivine (SCO) differ by ~10
187 ppm on our setup. This result disagrees with that of (Pack and Herwartz, 2014), which showed
188 only a 1 ppm difference between these standards. Considering that our SCO sample (SCO99-olv)
189 may differ from that of other laboratories and that our measured compositions of SCO yield more
190 variability than our measurements of UWG-2, we use UWG-2 as the primary standard. Further
191 scaling of the triple-oxygen results is done by assigning a fixed difference in oxygen isotope
192 compositions between Air-O₂ and UWG-2. The values used are $\Delta(\delta^{18}\text{O})_{\text{Air} - \text{UWG-2}} = 17.4\text{‰}$,
193 consistent with PBL corrected measurements from our laboratory and $\Delta(\Delta^{17}\text{O})_{\text{Air} - \text{UWG-2}} = -$

194 0.421‰ which is consistent with previously published values corrected to VSMOW2-SLAP
195 scaling (Yeung et al., 2018). This scheme yields inter-laboratory agreement in standard materials
196 within 10 ppm for $\Delta^{17}\text{O}$ (Yeung et al., 2018).

197
198 **3. Results:**
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200
201 **Fig. 1.** Oxygen triple-isotope composition of cherts through time. **a.** Measured $\Delta^{17}\text{O}$ of cherts
202 analyzed for this study. Point size is plotted to the precision of the measurement ($0.004\text{‰ } 1\sigma$). **b.**
203 Measured $\delta^{18}\text{O}(=\ln[\delta^{18}\text{O}+1])$ of cherts analyzed for this study. Uncertainties for $\delta^{18}\text{O}$ (0.08‰)
204 are smaller than the point size.

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206

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

208

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

209
210 The cherts show a trend of increasing $\delta^{18}\text{O}$ and decreasing $\Delta^{17}\text{O}$ values through time
211 (Fig.1 and Table 1). The total range in $\Delta^{17}\text{O}$ values is approximately 0.1‰, with an average
212 decrease of 0.02‰ per billion years. Phanerozoic marine cherts are characterized by $\lambda = 0.5223$
213 ± 0.0014 (1σ ; the slope of a $\delta^{17}\text{O}$ vs. $\delta^{18}\text{O}$ cross-plot), and Precambrian cherts by $\lambda = 0.5263 \pm$
214 0.0006 . These λ values suggest that different processes and/or reservoirs govern oxygen triple-
215 isotope variations in Phanerozoic and Precambrian cherts. Where repeat analyses were done
216 (majority of samples; see supplemental) different analyses of the same band or region of the
217 cherts yields nearly equivalent results, indicating homogeneity of oxygen isotopes in these
218 samples at spatial scales greater than our sampling scale ($\sim 1 \text{ mm}^3$). Our choice to use the pooled
219 variance of these analyses for our analytical uncertainty means that any homogeneity at this scale
220 is factored into our uncertainty ($\pm 0.004\text{‰}$ for $\Delta^{17}\text{O}$ and $\pm 0.08\text{‰}$ for $\delta^{18}\text{O}$).

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225 **4. Discussion**

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227 **4.1 Phanerozoic cherts**

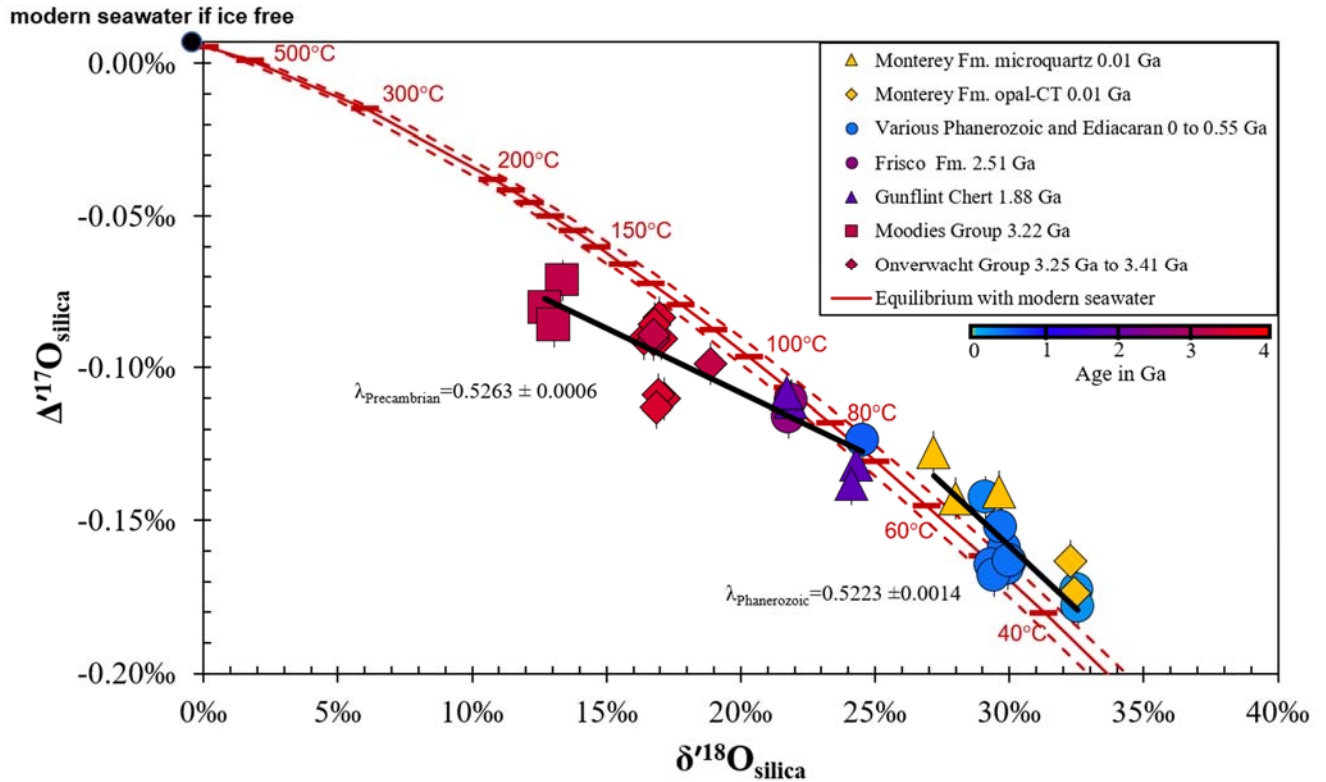


Fig. 2. $\delta^{18}\text{O}$ vs. $\Delta^{17}\text{O}$ of cherts and two Neogene Opal-CT samples. Uncertainties are the same as in Fig. 1. The red curve is the range of silica triple-oxygen isotope compositions compatible with formation in the modern ice-free ocean [$\delta^{18}\text{O} = -1\text{‰}$, $\Delta^{17}\text{O} = 0.0075\text{‰}$ 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 $\pm 1\text{‰}$ from a modern ice-free ocean.

228

The oxygen-isotope compositions of chert and opal-CT in the Miocene Monterey

229

Formation (0.01 Ga) are consistent with growth from a water that has a composition offset from

230

a modern (ice-free) ocean by either +1.5‰ in $\delta^{18}\text{O}$, +0.008‰ in $\Delta^{17}\text{O}$, or some intermediate

231

composition within those bounds (see Fig. 2). This difference could be explained by slight

232 analytical differences between our calibration and that used for the silica-water fractionation
233 curve (Sharp et al., 2016; Wostbrock et al., 2018). Therefore, the growth waters for these cherts
234 are isotopically indistinguishable from ice-free modern seawater (hereafter “isotopically
235 modern” seawater), although a small porewater oxygen-isotope change during chert diagenesis
236 cannot be ruled out. The Miocene opal and chert compositions are plausibly explained by an
237 open seawater-porewater system that recrystallizes silica at various temperatures during burial.
238 This interpretation is consistent with previous work on silica (Murata et al., 1977) and carbonates
239 (Loyd et al., 2012) in diagenetic settings that showed little evidence for significant porewater
240 $\delta^{18}\text{O}$ evolution. We thus interpret the λ value of 0.5223 from the Miocene cherts to result from
241 chert recrystallization in pore waters of constant isotopic composition over a range of
242 temperatures. For this environment, the diagenetic fluid appears to be a proxy for the isotopic
243 composition of coeval seawater.

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

255 and (2) the oxygen isotope composition of seawater has remained roughly constant since at least
256 the Ordovician. This latter interpretation corroborates recent carbonate clumped-isotope results,
257 which suggest a seawater $\delta^{18}\text{O}$ value bound within $\sim 2\text{‰}$ since the Cambrian (Coogan et al.,
258 2019; Cummins et al., 2014; Henkes et al., 2018; Ryb and Eiler, 2018).

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

269

270 **4.2 Precambrian Cherts**

271 Unlike for the Phanerozoic cherts, the oxygen-isotope compositions of the Latest
272 Archean and Proterozoic cherts require diagenetic recrystallization at higher temperatures (70-
273 90°C) and/or in isotopically different waters from those of the Phanerozoic. Paleoarchean cherts
274 cannot have formed in isotopically modern seawater, invalidating an early hypothesis that they
275 had grown at elevated temperatures from such fluids (Knauth and Lowe, 2003). Potential
276 explanations for triple-oxygen compositions of Precambrian cherts involve scenarios in which (i)
277 the initial growth fluids had a different isotopic composition, (ii) the cherts are internally mixed,

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

282

283 **4.2.1 Scenarios 1 and 2: Early diagenesis in low- $\delta^{18}\text{O}$, high- $\Delta^{17}\text{O}$ fluids**

284 If the early diagenesis of Phanerozoic cherts is a satisfactory model, i.e., recrystallization
285 occurred between 35°C and 60°C, then one can estimate the fluid composition required to
286 precipitate Precambrian cherts in that environment. Using this approach, the oxygen triple-
287 isotope composition of Onverwacht Group cherts ($\delta^{18}\text{O} = 17.165\text{‰}$, $\Delta^{17}\text{O} = -0.090\text{‰}$ on
288 average) imply a diagenetic fluid of $\delta^{18}\text{O} = -16.4\text{‰}$ to -10.7‰ and $\Delta^{17}\text{O} = 0.103\text{‰}$ to 0.057‰
289 for the Paleoproterozoic. Under this interpretation, younger cherts are compatible with growth in
290 fluids that were isotopically closer to modern seawater, but those fluids still must have lower
291 $\delta^{18}\text{O}$ and higher $\Delta^{17}\text{O}$ values. The origins of these low- $\delta^{18}\text{O}$, high- $\Delta^{17}\text{O}$ fluids is enigmatic; we
292 explore the possibility that lighter diagenetic fluids represent (1) meteoric waters and (2) coeval
293 seawater.

294 The Precambrian cherts can be described by a singular trend different from the
295 Phanerozoic cherts, with a λ value of 0.5263. This λ value is indistinguishable from that
296 characterizing meteoric waters with $\delta^{18}\text{O} > -20\text{‰}$ [$\lambda = 0.5265 \pm 0.0003$; (Sharp et al., 2018)]. A
297 possible explanation for the compositions of Precambrian cherts is thus subsurface intrusion of
298 meteoric waters into the early diagenetic environment where they recrystallized. The isotopically
299 lightest cherts presented here would require nearly pure meteoric waters with low $\delta^{18}\text{O}$ values \leq
300 -11‰ if water-to-rock ratios are high. Explaining the temporal trend in triple-oxygen

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

306 However, it is clear from studies of the Paleoproterozoic cherts of the Onverwacht Group
307 (3.41 Ga to 3.25 Ga; plotted as diamonds in Figure 2) and the Buck Reef chert in particular
308 (BRC; 3.41 Ga), that at least some Paleoproterozoic cherts underwent early diagenetic
309 recrystallization in an environment similar to that for the Phanerozoic cherts (Knauth and Lowe,
310 2003). The lines of supporting evidence include: the range of $\delta^{18}\text{O}$ values matching the $\sim 7\text{‰}$
311 range of Phanerozoic cherts (despite lower mean values), the apparent early silicification and
312 brecciation of “white cherts” of the BRC and Mendon Formation, and silicification prior to the
313 compaction of carbonaceous particles and relicts of opal-CT lepispheres (Hren et al., 2009;
314 Knauth and Lowe, 2003; Stefurak et al., 2015; Tice and Lowe, 2006; Trower and Lowe, 2016).
315 Furthermore, the chert shows no evidence for exogenous inputs from meteoric waters based on
316 $\delta\text{D}-\delta^{18}\text{O}$ trends, which are more consistent with early diagenesis at temperatures below 55°C
317 (Hren et al., 2009). The recrystallization fluid for the samples in that study were thus interpreted
318 to be coeval diagenetic fluids.

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

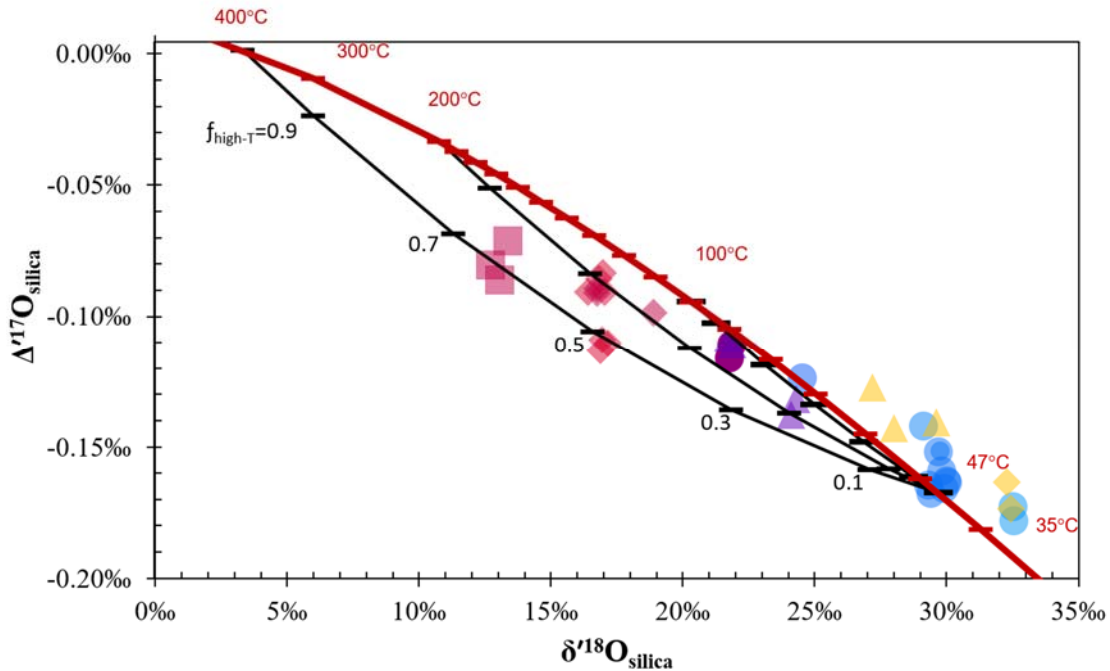
324 and $\Delta^{17}\text{O} = 0.092\text{‰}$ to 0.044‰ , still different from isotopically modern seawater. Note that the
325 white chert from the BRC analyzed here has a lower $\delta^{18}\text{O}$ (16.9‰) than equivalent samples
326 from the previous study, with a composition closer to the black cherts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

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

339

340

341 **4.2.2 Scenario 3: Mixtures of high- and low-temperature phases**



342

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

349

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

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

359 If the cherts analyzed here are mixtures of high- and low-temperature silica, the
360 heterogeneity would need to manifest at a scale $<1 \text{ mm}^3$, perhaps at the scale of microquartz grains
361 (10^{-5} mm^3). Microanalytical techniques may be able to test this hypothesis. A broad distribution in
362 $\delta^{18}\text{O}$ has been observed in some Precambrian cherts, particularly those of the 1.88 Ga Gunflint
363 Formation, examples of which were also analyzed here (triangles in Figures 2 and 3). Previous
364 work indicated an isotopic heterogeneity of $\sim 12\text{‰}$ at a $2 \mu\text{m}$ scale in the Gunflint chert, which was
365 taken as evidence for the presence of a $\sim 130^\circ\text{C}$ hydrothermal silica mixing endmember (Marin et
366 al., 2010). Mixing between a high-temperature silica endmember at 120°C ($\sim 40\%$) and a low-
367 temperature silica endmember at 47°C ($\sim 60\%$), both formed in isotopically modern seawater, can
368 explain the triple-oxygen composition of our Gunflint chert samples. However, this particular
369 mixture is not unique; there exists a continuum of scenarios for two-endmember (high- and low-
370 temperature silica) mixtures that can explain these samples if the oxygen-isotope composition of
371 the growth fluid is allowed to vary. For example, a difference in $\delta^{18}\text{O}$ of 12‰ can also be attained
372 if the two end members formed in the same water at temperatures of $\sim 20^\circ\text{C}$ and $\sim 70^\circ\text{C}$, as is
373 reasonable for the early diagenetic environment. This particular scenario is compatible with water
374 compositions of $\delta^{18}\text{O} < -4\text{‰}$ using the bulk oxygen isotope compositions of Gunflint chert
375 measured here.

376

377

378 **4.2.3 Scenario 4: Late, closed-system recrystallization of silica**

379

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

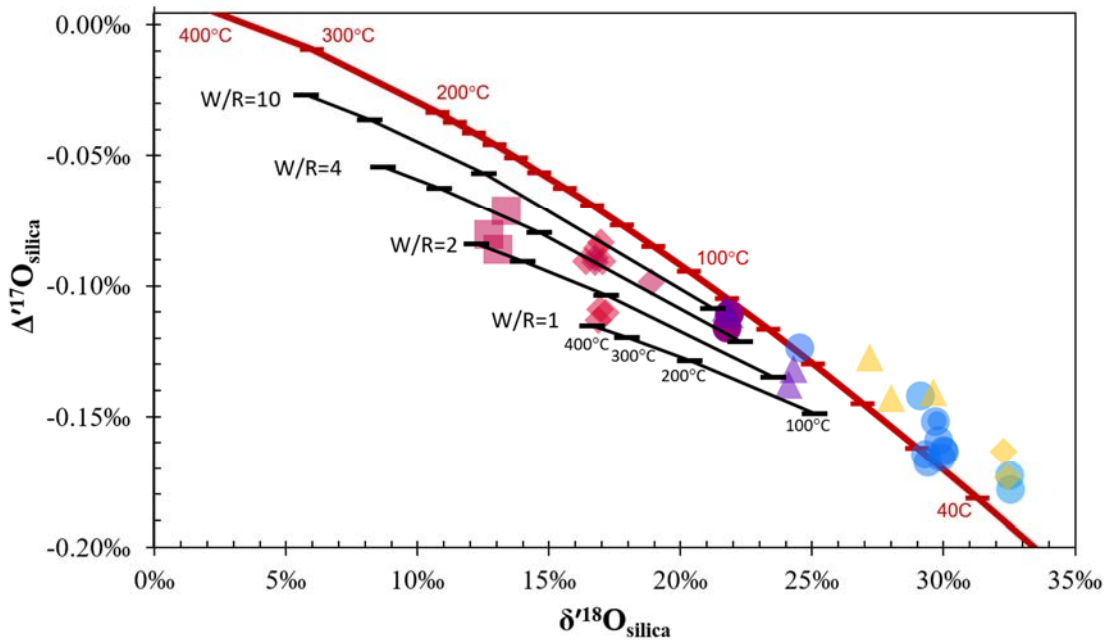
384

385

386
$$\left(\frac{W}{R}\right) R_{w,i} + R_{r,i} = R_{w,f} \left[\alpha + \left(\frac{W}{R}\right)\right] \quad \text{Eq.1}$$

387

388 where R is the ratio of the heavy isotope to the light isotope, i.e., $^{17}\text{O}/^{16}\text{O}$ or $^{18}\text{O}/^{16}\text{O}$, α is the
389 temperature dependent fractionation factor for the rock (SiO_2) relative to water, the subscripts w
390 and r indicate the parameters for water and rock, respectively, and the subscripts i and f indicate
391 initial and final compositions, respectively. W and R are the amounts of oxygen held in water and
392 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 Paleoarchean
428 diagenetic fluids. Here, we use the interpretation that the BRC represents a diagenetic sequence

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

441
442 The cherts of the Onverwacht Group have been interpreted as marine due to the large lateral
443 extent of the chert units, the need for large amounts of silica to account for hundreds of meters of
444 silicified rocks and the presence of evaporites (indicating a saline environment). Thus, interpreting
445 the chert growth waters as the coeval diagenetic fluid leads naturally to the interpretation that
446 seawater in the Archean was significantly isotopically lighter. If the diagenetic fluid approximates
447 coeval seawater for the Precambrian samples—as is case for Phanerozoic cherts—the triple-
448 isotope data suggest that seawater became progressively more ^{18}O -enriched over geologic time
449 (Fig. S1). Any feasible mechanisms for accomplishing a lower $\delta^{18}\text{O}$ for Paleoproterozoic seawater
450 require more intense low temperature water-rock interactions and/or less intense high temperature
451 water-rock interactions earlier in Earth's history (Jaffrés et al., 2007; Kasting et al., 2006; Pack

452 and Herwartz, 2014; Wallmann, 2004). Modeling studies suggest that a seawater $\delta^{18}\text{O}$ value of -
453 11‰ can only be achieved by dramatically reducing the proportion of water-rock interactions
454 occurring at high temperatures (Jaffrés et al., 2007; Kasting et al., 2006). Such a scenario could be
455 realized if submarine magmatic centers were shallower in the Archean, perhaps associated with
456 higher mid-ocean ridge crests or more extensive volcanic plateaus (Kamber, 2010; Kasting et al.,
457 2006; Lambert, 1980). Alternatively, a more sluggish tectonic regime in the Archean (Tang et al.,
458 2016), characterized by a reduced area of magmatic activity, could lead to a reduction in high-
459 temperature water-rock chemistry.

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

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

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

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

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

506

507 **5.1 Conclusions:**

508 The triple-oxygen isotope composition of marine cherts from 3.5 billion years of Earth's
509 history indicate a switch in some aspect of the factors leading to the oxygen isotope composition
510 of chert occurring at some time prior to the Ordovician. The oxygen isotope composition of
511 Phanerozoic cherts reflect recrystallization over a range of early diagenetic temperatures (35°C-
512 60°C) in a water indistinguishable from that of the modern ocean ($\delta^{18}\text{O} = 0 \pm 2\text{‰}$). Importantly,
513 the additional constraint provided by ^{17}O shows that low $\delta^{18}\text{O}$ values of Archean cherts are
514 incompatible with a hot (>70°C) surface and an isotopically modern oceans in the Archaean.
515 Geological and geochemical constraints from the literature implying an early diagenetic origin
516 for a subset of the measured Archean cherts, when combined with the data presented here,
517 suggests that at 3.45 Ga diagenetic fluids had a $\delta^{18}\text{O}$ value of < -11‰, with surface temperatures
518 <34°C. While this result may be used to indicate a secular evolution of seawater $\delta^{18}\text{O}$, alternate

519 feasible explanations for the chert compositions remain which do not require a change in
520 seawater $\delta^{18}\text{O}$.

521

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530 Hayles and Hehe Jiang. All authors contributed to interpretations.

531

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