

Triple oxygen isotope evidence for a hot Archean ocean

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ABSTRACT

Triple oxygen isotope ($\delta^{17}\text{O}$ and $\delta^{18}\text{O}$) values of high- and low-temperature altered oceanic crust and products of basalt alteration experiments were measured to better constrain ocean isotope compositions in deep time. The data define an array of $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ ($\Delta^{17}\text{O} = \delta^{17}\text{O} - \lambda_{\text{RL}} \times \delta^{18}\text{O} + \gamma$) values from mantle values toward 1‰ and −0.01‰, respectively, with a λ of ~0.523. The altered oceanic crust data were used to construct a model for estimating $\delta^{18}\text{O}$ – $\Delta^{17}\text{O}$ values of the ancient oceans if the continental weathering flux (F_{CW}) and/or hydrothermal oceanic crust alteration flux (F_{HT}) changed through time. A maximum lowering of 7‰ and 4‰, respectively, is achieved in the most extreme cases. The $\delta^{18}\text{O}$ value of the ocean cannot be raised by more than 1.1‰. Eclogites from the Roberts Victor kimberlite (South Africa), with a protolith age of 3.1 Ga, have $\delta^{18}\text{O}$ – $\Delta^{17}\text{O}$ values that precisely overlap with those of the modern altered oceanic crust, suggesting that the Archean oceans had similar isotope values as today. Published triple isotope data for Archean cherts show that all samples have been altered to some degree and suggest an Archean ocean surface temperature of ~70–100 °C. An ocean as light as −2‰ is still consistent with our eclogite data and reduce our temperature estimates by 10 °C.

INTRODUCTION

Some of the best constraints on Earth's surface temperature in deep time come from oxygen isotope studies of Archean sedimentary chert. The oxygen isotope fractionation between silica and water ($\delta^{18}\text{O}_{\text{silica}} - \delta^{18}\text{O}_{\text{water}}$) is temperature dependent but requires an accurate estimate for the $\delta^{18}\text{O}$ value of the ancient seawater in which the silica formed as well as the degree of post-

depositional diagenesis [$\delta = \left(\frac{R_x}{R_{\text{std}}} - 1 \right) \times 1000$;

R is the ratio of the heavy to light isotope of the sample (R_x) and standard (R_{std})]. Due to the inability to constrain these parameters, published conclusions on Archean ocean temperatures are, not surprisingly, quite varied. Some have suggested ancient ocean temperatures of 70 °C or more (Knauth and Epstein, 1976; Knauth and Lowe, 1978; Tartèse et al., 2017; Garcia et al., 2017). Others have proposed temperatures similar to that of the modern ocean (Krissansen-Totton et al., 2018) with low $\delta^{18}\text{O}$ ocean water values (Wallmann, 2001; Kasting et al., 2006).

Others argue that all Archean sediments have undergone some diagenesis, such that information about ancient paleoclimate is not preserved.

Information from the $^{17}\text{O}/^{16}\text{O}$ isotope ratio adds an additional constraint to paleotemperature estimates. The triple oxygen isotope system ($\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values) allows us to better identify and potentially “see through” diagenesis to estimate the pristine sedimentary isotope ratio and hence temperatures of formation (e.g., Herwartz et al., 2015; Wostbrock et al., 2020). This concept is predicated on knowing the oxygen isotope ratio of the ancient ocean, which is unconstrained using $\delta^{18}\text{O}$ values alone. The $\delta^{18}\text{O}$ value of the ocean is thought to be buffered by a combination of high-temperature seafloor hydrothermal alteration and low-temperature continental and submarine weathering (Muehlenbachs, 1998). Changes in the ratio of high- to low-temperature alteration processes would change the $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values of the ocean.

We measured the triple oxygen isotope composition of altered oceanic lithosphere and the products of high-temperature basalt-seawater

exchange experiments to estimate how the calculated $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values of the ocean are modified with changing high- and low-temperature alteration fluxes (e.g., Sengupta and Pack, 2018). The modern altered oceanic crust data were then compared with those from eclogite samples (RVE) from the Roberts Victor kimberlite (South Africa), which has a protolith age of 3.1 Ga (Gonzaga et al., 2010). Similar triple isotope values for the eclogite xenoliths and modern altered crust would indicate that the eclogite xenolith isotope values are inherited from hydrothermal alteration. The triple isotope range of eclogite values compared to those of modern altered crust then provides a constraint on the isotopic composition of the ocean at 3.1 Ga. Finally, the published triple isotope values for Archean cherts were used to constrain surface temperatures of the ancient oceans.

TRIPLE OXYGEN ISOTOPE COMPOSITION OF ALTERED OCEANIC CRUST AND THE ROBERTS VICTOR ECLOGITE

Triple oxygen isotope measurements were made on whole rock and mineral separates from high-temperature-altered Integrated Ocean Drilling Program Hess Deep plutonic cores, low-temperature-altered basalts from Deep Sea Drilling Project Holes 504B and 417A, mineral separates from a dredged basalt from the Mid-Atlantic Ridge (dredged by the Canadian Oceanographic Service), experimental run products of basalt reacted with seawater at 300 °C to 500 °C (Cole et al., 1987), and Roberts Victor eclogite mantle xenolith mineral separates (data are provided in Tables S1–S5 in the Supplemental Material¹). High-temperature-altered crust samples show a slightly concave-upward trend of

¹Supplemental Material. Sample descriptions, analytical methods, definitions, isotope data, and a description of the mass balance model. Please visit <https://doi.org/10.1130/G50230.1> to access the supplemental material, and contact editing@geosociety.org with any questions.

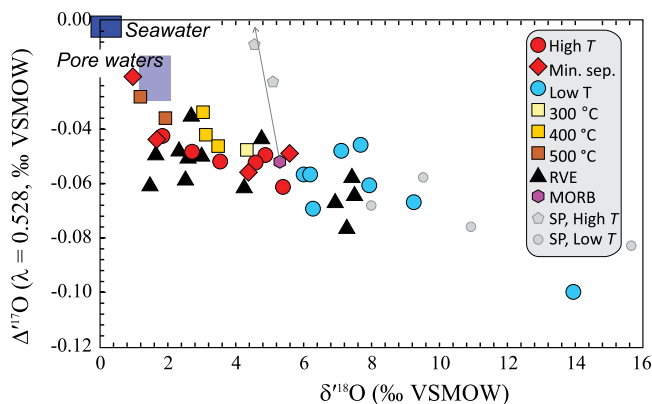


Figure 1. Triple oxygen isotope composition ($\Delta^{17}\text{O}$ versus $\delta^{18}\text{O}$) of altered oceanic crust (circles, diamonds), basalt alteration experiments (squares), and Roberts Victor eclogite (RVE; South Africa) (triangles). Data not from our study are from Sengupta and Pack (2018), Shanks (2001), Lloyd et al. (2019), and Zakharov et al. (2021). VSMOW—Vienna standard mean ocean water; T—temperature; Min. sep.—mineral separates; MORB—mid-ocean ridge basalt; SP—data from Sengupta and Pack (2018). Data are plotted as averages. Arrow is SP high-T alteration trend. See the Supplemental Material (see footnote 1) for sample details.

MORB—mid-ocean ridge basalt; SP—data from Sengupta and Pack (2018). Data are plotted as averages. Arrow is SP high-T alteration trend. See the Supplemental Material (see footnote 1) for sample details.

decreasing $\delta^{18}\text{O}$ and increasing $\Delta^{17}\text{O}$ (see the Supplemental Material for definitions of $\Delta^{17}\text{O}$ and λ) from typical mantle values, approaching $\delta^{18}\text{O} = 1\text{‰}$ and $\Delta^{17}\text{O} = -0.01\text{‰}$ with

$$\lambda = 0.523 \pm 0.002 \quad (\lambda_{A-B} = \frac{\delta^{17}\text{O}_A \delta^{17}\text{O}_B}{\delta^{18}\text{O}_A \delta^{18}\text{O}_B} \text{ for}$$

phases A and B) (Fig. 1). This alteration trend toward ocean water values is expected, given the small isotope fractionation between basalt and water at 300–500 °C (Bowers and Taylor, 1985; Cole et al., 1987). Correspondingly, the isotopic compositions of hydrothermal vent fluids increase from approximately $\delta^{18}\text{O} = 0\text{‰}$ and $\Delta^{17}\text{O} = 0\text{‰}$ (modern seawater) toward $\delta^{18}\text{O} = 1\text{‰}$ – 2‰ and $\Delta^{17}\text{O} = -0.01\text{‰}$ (pore-water values from Shanks [2001], Lloyd et al. [2019], and Zakharov et al. [2021]). The present results contrast with previous triple isotope measurements for high-temperature-altered oceanic crust, which show a significantly steeper alteration trend of $\lambda = 0.470$ (Fig. 1) in triple oxygen isotope space toward $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values of $\sim 4\text{‰}$ and 0‰ , respectively (Sengupta and Pack, 2018). Results from the experimentally altered basalts exchanged with seawater show the same trend as natural altered basalt samples (Fig. 1), indicating approximate alteration temperatures for Hess Deep samples of ~ 300 – 400 °C.

Low-temperature-altered basalts trend toward increasing $\delta^{18}\text{O}$ and decreasing $\Delta^{17}\text{O}$ from pristine mid-ocean ridge basalt (MORB) ($\lambda = 0.523 \pm 0.001$) due to the larger isotope fractionations at low temperatures (Fig. 1). Our data agree well with those of Sengupta and Pack (2018).

It has been proposed that Roberts Victor eclogite xenoliths preserve the oxygen isotope composition of an Archean (2.7–3.1 Ga; Gonzaga et al., 2010; Shirey et al., 2005) altered oceanic crustal protolith (MacGregor and Manton, 1986; Radu et al., 2019; Hardman et al., 2021). We find that the combined $\delta^{18}\text{O}$ – $\Delta^{17}\text{O}$ values for Roberts Victor eclogite samples overlap the

field of modern altered oceanic crust with a nearly identical λ value of 0.524 ± 0.003 (Fig. 1), supporting this assumption. The range of $\delta^{18}\text{O}$ values measured by Radu et al. (2019) for Roberts Victor eclogite agree with those of the modern altered oceanic crust except for one corundum-bearing sample that is $\sim 1\text{‰}$ lighter than modern altered values. This is expected for an ice-free (-1‰) ocean. Our near-modern $\delta^{18}\text{O}$ values are supported by an oxygen isotope study of a 3.8 Ga ophiolite (Furnes et al., 2007).

CONTROLS ON THE ISOTOPIC COMPOSITION OF THE OCEAN

Expansion of oxygen isotope analyses to include the rare ^{17}O isotope introduces a second mass-dependent fractionation constraint on the marine sediment secular trend. The conclusions reached from recent triple oxygen isotope studies of Archean cherts are nevertheless varied and include the following: (1) ancient ocean had $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values that were similar to those of the modern ice-free Earth and ocean temperatures ranging from 66 to 76 °C or greater (Sengupta and Pack, 2018; Lowe et al., 2020); (2) the isotopic composition of ancient cherts were altered by interaction with a meteoric fluid (Liljestrand et al., 2020; Sengupta et al., 2020); (3) some ancient chert deposits have quartz that precipitated at temperatures between 150 and 170 °C with hydrothermal vent fluids (Zakharov and Bindeman, 2019; Zakharov et al., 2021); and (4) high atmospheric $p\text{CO}_2$ and higher silicification and carbonization fluxes resulted in a low $\delta^{18}\text{O}$ value for the ocean and only moderately warm ocean temperatures (Herwartz et al., 2021).

How variable the oxygen isotope composition of the ocean is through time is a crucial parameter in all of these studies. Mass-balance models have been used to explain the oxygen isotope composition of the modern ocean and to determine whether the oxygen isotope composition of ancient oceans was lower than modern (Muehlenbachs, 1998; Wallmann, 2001; Jaffrés

et al., 2007; Sengupta and Pack, 2018; Herwartz et al., 2021). These models consider the processes of high-temperature oceanic crust alteration, low-temperature oceanic crust alteration, continental weathering, continental growth, and mantle recycling of water, which collectively buffer the isotopic composition of the oceans. Alteration of these fluxes could explain the low $\delta^{18}\text{O}$ values of Archean cherts (Wallmann, 2001; Kasting et al., 2006).

This study revisits the triple oxygen isotope buffering model with a substantial data set for modern altered oceanic crust. The ocean buffering mass-balance model considers the flux F (oxygen exchanged in g/yr) of each rock-seawater interaction process and the corresponding $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ fractionations between unaltered and altered lithospheric reservoirs (see Table S6 for model equations). The model accurately predicts a modern seawater $\delta^{18}\text{O} = -0.29\text{‰} \pm 0.08\text{‰}$ and $\Delta^{17}\text{O} = -0.002\text{‰} \pm 0.0003\text{‰}$, with high-temperature alteration (HT) and continental weathering (CW) each accounting for $\sim 37\%$ of all O isotopes exchanged.

The feasibility of having light Archean seawater can be tested by modifying the fluxes (F) of the model. F_{HT} would be less in geological times with lower sea levels or greater rates of seafloor spreading, and different weathering conditions due to increased land vegetation and higher $p\text{CO}_2$ would change F_{CW} (Walker and Lohmann, 1989; Wallmann, 2001; Kasting et al., 2006; Jaffrés et al., 2007; Herwartz et al., 2021). The effects of modifying these fluxes (F_{CW} and F_{HT}) can be seen in Figure 2. Decreasing F_{HT} leads to minimum seawater $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values of -4.1‰ and 0.014‰ , respectively (for complete shutoff). Increasing F_{CW} by a factor of $100 \times$ results in a lower seawater $\delta^{18}\text{O}$ value of -7.0‰ . A more reasonable $10 \times$ increase reduces the $\delta^{18}\text{O}$ value to -3.6‰ , significantly higher than postulated values as light as -13.3‰ (Jaffrés et al., 2007) and -10‰ (Kasting et al., 2006). The heaviest seawater $\delta^{18}\text{O}$ value from the model results when F_{HT} is increased by $100 \times$ and equals 1.1‰ with a corresponding $\Delta^{17}\text{O}$ of -0.006‰ , significantly less than the 3.3‰ proposed for Archean seawater by Johnson and Wing (2020).

ARCHEAN OCEANS

Assuming that fluxes were different in ancient times, a reasonable range of triple oxygen isotope compositions of the ancient ocean can be estimated using the λ values for changes in F_{HT} and F_{CW} . When these are combined with measured triple isotope data for Archean cherts, Archean ocean temperatures can be estimated.

We start with the assumption that the isotopic composition of the ocean was similar to modern, a conclusion based on the Roberts Victor eclogite data and previous results from Furnes et al. (2007). We then consider an Archean Earth

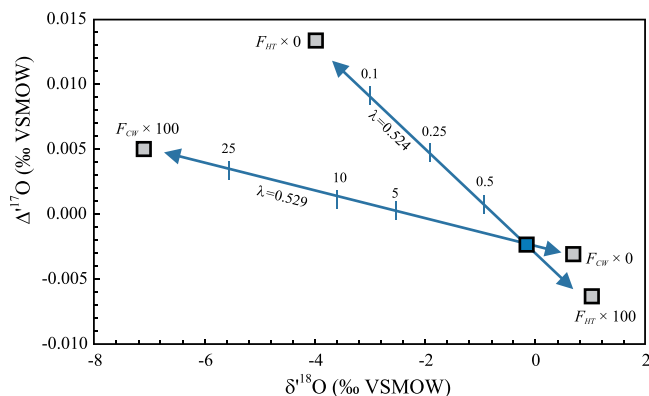


Figure 2. Evolving seawater compositions with varying high-temperature alteration (F_{HT}) and continental weathering (F_{CW}) fluxes. Blue square represents modeled ice-free seawater; gray squares represent model-generated seawater compositions with extreme endmember F_{HT} and F_{CW} rates.

environment where F_{HT} is lower due to shallower ocean depths and, finally, conditions where F_{CW} is larger than modern estimates due to increased pCO_2 and easily weathered greenstones.

Figure 3A plots the measured triple isotope compositions of Archean cherts (Liljestrاند et al., 2020; Sengupta et al., 2020; Lowe et al., 2020) and the equilibrium SiO_2 - H_2O fractionation curves (Sharp et al., 2016) for ice-free seawater ($\delta^{18}O = -1\text{‰}$). Only the 3.4 Ga Barberton Greenstone Belt (South Africa) samples (Lowe et al., 2020) plot close to the equilibrium curve and correspond to temperatures of $\sim 120^\circ\text{C}$. Lowe et al. (2020) stated that these samples have probably undergone minor diagenesis and that the pristine samples likely had

$\delta^{18}O$ values closer to 23‰ – 24‰ , as determined by high-spatial-resolution ion microprobe data (Stefurak et al., 2015). A 24‰ chert precipitating in equilibrium with seawater plots on the equilibrium curve (blue triangle, Fig. 3) with a corresponding formation temperature of 77°C . This compares well with independent estimates of $>70^\circ\text{C}$ from Si isotope ratios (Robert and Chaussidon, 2006). Assuming a lower ocean value of -2‰ (approximate uncertainty based on Roberts Victor eclogite samples) reduces the estimated ocean temperature by 10° to $\sim 67^\circ\text{C}$.

The majority of the altered Barberton samples can be explained by 120 – 200°C diagenesis and/or metamorphism through exchange with a water with oxygen isotope values similar to

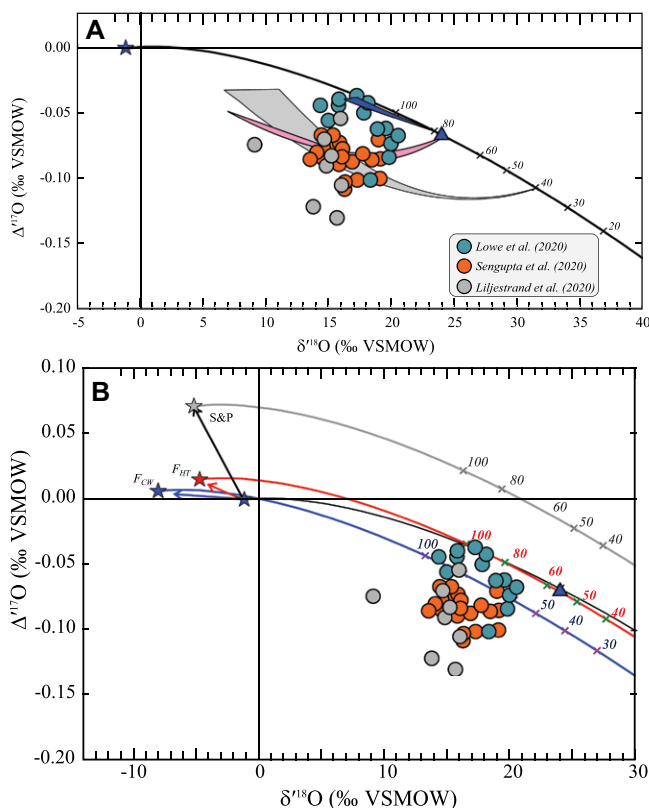


Figure 3. Isotopic composition ($\delta^{18}O$ vs $\Delta^{17}O$) of Archean cherts and silica-water equilibrium scale. (A) Chert data are from Lowe et al. (2020), Sengupta et al. (2020), and Liljestrاند et al. (2020). Blue triangle is hypothetical “pristine” sample (Stefurak et al., 2015) suggesting $\sim 80^\circ\text{C}$ ocean temperatures. Lower $\delta^{18}O$ values can be explained by closed-system mineral reequilibration (blue curve). Pink field illustrates exchange with evaporated fluid ($\delta^{18}O = -5\text{‰}$; $\Delta^{17}O = -0.03\text{‰}$). Gray field is diagenetic pathway assuming initial heavy $\delta^{18}O$ chert exchanged with light fluid ($\delta^{18}O = -10\text{‰}$; $\Delta^{17}O = +0.03\text{‰}$). (B) Equilibrium curves for hypothetical light oceans due to increased continental weathering (blue; flux F_{CW}), decreased high-temperature alteration (red; F_{HT}), and previous estimate (gray; Sengupta and Pack, 2018 [S&P]). Stars represent modeled

end-member seawater compositions. Numbers along equilibrium curves are temperatures of equilibration in $^\circ\text{C}$. VSMOW—Vienna standard mean ocean water.

those of the ocean, or simply reequilibration with other phases such as calcite, iron oxides, and clay minerals (blue curve and triangle, Fig. 3).

The results from two other studies (Liljestrاند et al., 2020; Sengupta et al., 2020) include samples from the Barberton Greenstone Belt and Australian Pilbara craton. Both data sets lie significantly below the equilibrium fractionation line suggestive of more extensive diagenesis (Wostbrock et al., 2020). There are multiple diagenetic conditions that can explain the data, and two examples are given here. The first is if samples formed at a much lower formation temperature of $\sim 40^\circ\text{C}$, followed by interaction with a very light meteoric water ($\delta^{18}O = -10\text{‰}$, $\Delta^{17}O = 0.03\text{‰}$) (gray trajectory in Fig. 3A). However, a 40°C ocean is incompatible with the Lowe et al. (2020) data. A more reasonable explanation is that the samples formed at $\sim 80^\circ\text{C}$ and isotopically exchanged with an evaporated fluid with low $\Delta^{17}O$ values (e.g., Passey and Levin, 2021). This trajectory is shown by the pink field in Figure 3A.

Finally, the case where the $\delta^{18}O$ values of the ancient oceans were lighter than today is considered (Fig. 3B). The red curve is for a light ocean due to a reduced F_{HT} , the blue curve is for increased F_{CW} , and the gray curve is the predicted end-member change in ocean water by Sengupta and Pack (2018). The blue curve (increased F_{CW}) lies below the majority of the Lowe et al. (2020) data, which cannot easily be explained by any reasonable alteration scenario. Similarly, the Sengupta and Pack (2018) curve lies far above all measured data due to a steeper $\lambda = 0.510$, and diagenetic mixing models cannot explain the measured data. The red curve (decreased high-temperature alteration) plots on top of the modern ocean value (dashed curve) with resulting temperatures $\sim 20^\circ\text{C}$ lower. This curve can explain the measured chert data, but the low $\delta^{18}O$ is at odds with the evidence for a modern ocean value due to the significant overlap between modern altered crust samples and the Archean Roberts Victor eclogite data (Fig. 1).

CONCLUSION

The triple oxygen isotope values of high- and low-temperature altered oceanic crust pass through the MORB value with a slight concave-upward trend, reaching $\delta^{18}O$ and $\Delta^{17}O$ values of $\sim 1\text{‰}$ and -0.01‰ , respectively, for the most high-temperature altered basalts and 9‰ and -0.06‰ , respectively, for most of the low-temperature altered basalts (one sample with $\delta^{18}O = 14.3$, $\Delta^{17}O = -0.100$). Data from high-temperature alteration experiments give similar results. The best-fit reduced high-temperature flux λ value of 0.524 ± 0.003 is significantly higher than a previous estimate ($\lambda = 0.510$; Sengupta and Pack, 2018), leading to lower $\Delta^{17}O$ for a correspondingly low- $\delta^{18}O$

ocean. Samples of Roberts Victor eclogite xenoliths with a 3.1 Ga protolith age define an array of $\delta^{18}\text{O}$ - $\Delta^{17}\text{O}$ values that overlap the modern altered oceanic crust data, providing confirmatory evidence of the altered crustal protoliths for these mantle samples and, more significantly, suggesting that the $\delta^{18}\text{O}$ value of the Archean ocean was similar to that of today. Calculated ocean temperatures from chert samples, assuming an ocean $\delta^{18}\text{O}$ value of -1‰ , are $>77^\circ\text{C}$ (67°C assuming a -2‰ ocean), approaching 100°C if minimal alteration is assumed.

Low- $\delta^{18}\text{O}$ Archean oceans could have existed in the deep past due to some combination of increased continental weathering or reduced high-temperature hydrothermal alteration. Modifications to the major model fluxes can generate oceans with $\delta^{18}\text{O}$ values as light as -7.0‰ . Increased continental weathering alone is inconsistent with the measured data. A low- $\delta^{18}\text{O}$ ocean induced by reduced high-temperature alteration can explain the chert data and would indicate a 60°C ocean temperature. However, a low- $\delta^{18}\text{O}$ ocean is inconsistent with the Roberts Victor eclogite data. Our best estimate for the Archean ocean surface temperature is $\sim 80\text{--}100^\circ\text{C}$.

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