

## Warm Archean oceans reconstructed from oxygen isotope composition of early-life remnants

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### Abstract

Deciphering the surface conditions on the Earth during Archean times (> 2.5 billion years ago – Ga) is crucial to constrain the conditions that promoted the development of life. The progressive shift through time of the oxygen isotopic compositions of Precambrian siliceous sediments – the so-called cherts – has been interpreted as indicating a secular decrease of seawater temperature by 50–80 °C from the early Archean to the present-day. However, this interpretation has been questioned, notably because it assumes that the seawater oxygen isotopic composition has remained globally constant since 3.5 Ga, though this has never been tested by direct isotopic measurements on Archean samples. Here we report measurements of the oxygen isotopic composition of carbonaceous matter indigenous to Precambrian cherts up to *ca.* 3.5 Ga. These new results demonstrate that the oxygen isotope composition of seawater during most of the Precambrian remained around  $0 \pm 5\text{‰}$ , which is consistent with the composition of present day seawater. Combined with the chert oxygen isotope composition record, this indicates that *ca.* 3.5 Ga ago ocean bottom-water temperatures were ~50–60 °C higher than today.

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### Introduction

The oxygen isotopic composition (hereafter reported in ‰ using the delta notation,  $\delta^{18}\text{O}_{\text{sample}} = \left[ \frac{(^{18}\text{O}/^{16}\text{O})_{\text{sample}}}{(^{18}\text{O}/^{16}\text{O})_{\text{SMOW}}} - 1 \right] \times 1000$  where SMOW stands for the present day Standard Mean Ocean Water composition) of cherts has increased systematically during the last 3.5 Ga from ~20 ‰ to ~35 ‰ (Knauth

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and Epstein, 1976; Knauth and Lowe, 2003; Robert and Chaussidon, 2006). Based on the temperature-dependence of the oxygen isotopic fractionation between silica and water (Knauth and Epstein, 1976), this isotopic record implies that the formation temperature (*T*) of cherts decreased by 50–80 °C since Archean times, assuming that silica formed from water with a  $\delta^{18}\text{O}$  of ~0 ‰ (Knauth and Epstein, 1976; Knauth and Lowe, 2003; Robert and Chaussidon, 2006). While this assumption is consistent with  $\delta^{18}\text{O}$  values measured in *ca.* 3.8 Ga ophiolites (Pope *et al.*, 2012) and with geochemical models indicating that  $\delta^{18}\text{O}_{\text{seawater}}$  is buffered to around  $0 \pm 2\text{‰}$  within a few tens of million years (*e.g.*, Lécuyer and Allemand, 1999), this hypothesis of a near constant  $\delta^{18}\text{O}_{\text{seawater}}$  through time has never been tested by direct measurements on Precambrian samples.

Several arguments have been put forward challenging the interpretation of elevated surface *T* during Precambrian times. Isotopic exchange during diagenesis and chert alteration could have decreased the original  $\delta^{18}\text{O}_{\text{chert}}$ , for example. However, observations of large ranges of  $\delta^{18}\text{O}_{\text{chert}}$  values at the micrometre scale in individual quartz grains (*e.g.*, Marin-Carbonne *et al.*, 2012) showed that Precambrian cherts can preserve a record of their pristine O-isotope signature, with diagenetic effects resulting in a limited excess of ~15–20 °C on the crystallisation *T* calculated previously. Also, the chert O-isotope record of warm *T* during the Precambrian apparently conflicts with evidence for large scale glaciations, such as the 2.2–2.45 Ga Huronian glaciations (*e.g.*, Evans *et al.*, 1997; Young, 2014). Therefore, it has been argued that constraints for a constant  $\delta^{18}\text{O}_{\text{seawater}}$  over time were indirect and weak, and that the increase of  $\delta^{18}\text{O}_{\text{chert}}$  values since 3.5 Ga rather reflects a 10–15 ‰ increase of  $\delta^{18}\text{O}_{\text{seawater}}$ , with average surface *T* remaining around 15–30 °C (*e.g.*, Kasting *et al.*, 2006; Jaffrés *et al.*, 2007). To provide further constraints on this key issue, we have investigated chert-hosted biogenic carbonaceous remnants, whose O isotope composition is directly related to that of the water in which their precursor microorganisms thrived.

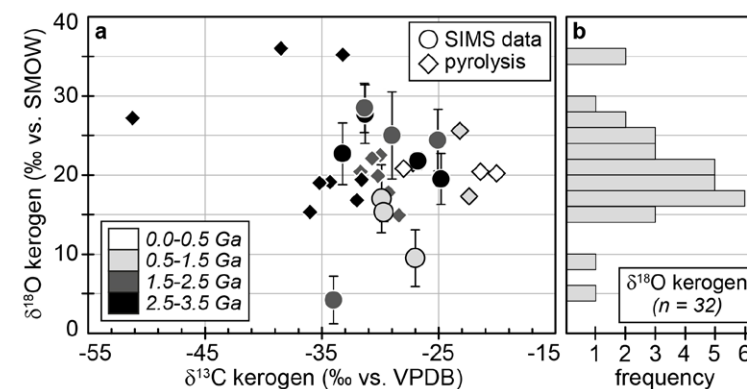
The isotopic composition of biomolecules is largely determined by metabolic exchange between living organisms and their environment. In aquatic heterotrophic organisms, for example, *ca.* 70–80 % of organic matter-derived oxygen originates from water (see Supplementary Information). In living organisms, fractionation of O isotopes between water and organic compounds results from both equilibrium and kinetic processes (*e.g.*, Schmidt *et al.*, 2015). As a result, different organic compounds are characterised by different O isotope compositions: oxygen is enriched in  $^{18}\text{O}$  by  $\sim 27 \pm 5\text{‰}$  compared to ambient water in carbohydrates such as cellulose, while it is enriched by  $\sim 19 \pm 3\text{‰}$  in carboxyl groups, for example (*e.g.*, Schmidt *et al.*, 2015). Chemical changes occurring during thermal maturation of organic matter (OM) may alter O isotope compositions of various organic compounds. O-rich thermolabile components (*e.g.*, carbohydrates and amino acids) are quickly degraded during maturation, resulting in residual OM (kerogen) dominated by resistant aromatic moieties in which O is mostly bound in hydroxyl (–OH), ketone (–C=O) and carboxyl (–COOH) functional groups (*e.g.*, De Gregorio *et al.*, 2011). Proto-kerogens derived from marine algae collected in recent surface sediments and isolated from Lower



Jurassic Toarcian shales are characterised by  $\delta^{18}\text{O}$  values that are on average  $20.5 \pm 1.1\text{‰}$  (2 SD) higher than the O isotope composition of waters in which the precursor biomass thrived (Supplementary Information). Such a  $\Delta^{18}\text{O}_{\text{kerogen-water}}$  is similar to our previous estimates (Tartèse *et al.*, 2016) and indicates that the O isotope composition of bulk immature kerogens is consistent with that of O bound to carboxyl functional groups, which appear to be one of the more resistant O-bearing functional group in thermally altered OM (*e.g.*, De Gregorio *et al.*, 2011). This suggests that oxygen in sedimentary OM preserves the  $\delta^{18}\text{O}$  signature of the carboxyl functional groups of its precursor biomass, which does not seem to be fractionated during maturation. Biogenic carbonaceous remnants have, therefore, a great potential to provide direct constraints on the O isotope composition of waters in which their precursor biomass lived.

### Oxygen Isotope Composition of Precambrian Kerogens

Bulk pyrolysis results obtained on 18 kerogens isolated from Precambrian cherts up to *ca.* 3.5 Ga have consistent  $\delta^{18}\text{O}$  values clustering around  $20 \pm 5\text{‰}$  (Wedeking, 1983) (Fig. 1 and Table S-1). To provide further constraints on the significance of bulk kerogen  $\delta^{18}\text{O}$  values, we used Secondary Ion Mass Spectrometry (SIMS) to analyse additional kerogens isolated by acid-maceration from cherts ranging in age from 0.58 to 3.42 Ga and affected by metamorphic conditions no higher than those of lower greenschist facies (Delarue *et al.*, 2016) (Supplementary Information). Bulk C isotope compositions of these kerogens are compatible with typical biological signatures ( $\delta^{13}\text{C}$  between  $-35$  and  $-25\text{‰}$ ; Fig. 1). Most kerogens have average SIMS  $\delta^{18}\text{O}$  values between *ca.* 15 and 25‰, which is consistent with values obtained by pyrolysis on bulk kerogens (Fig. 1). The kerogens older than 3.0 Ga analysed by SIMS have strikingly consistent average  $\delta^{18}\text{O}$  values between  $19.5 \pm 3.2$  and  $22.7 \pm 3.9\text{‰}$  (Table 1). In contrast, a few Proterozoic kerogens display large deviations from these older samples, with  $\delta^{18}\text{O}$  values ranging from  $4.2 \pm 3.0\text{‰}$  for the 1.88 Ga Gunflint samples to  $28.5 \pm 3.1\text{‰}$  for the 1.5 Ga Jixian sample (Table 1). Other samples, such as Bitter Springs (0.8 Ga), also display a low average  $\delta^{18}\text{O}$  value ( $8.6 \pm 3.7\text{‰}$ ), while average  $\delta^{18}\text{O}$  values of *ca.*  $25 \pm 5\text{‰}$  for the Naberru (1.85 Ga) and McArthur (1.6 Ga) kerogens are consistent within errors with those of Archean kerogens (Table 1). Finally, the average  $\delta^{18}\text{O}$  of  $17.0 \pm 4.3\text{‰}$  for the Ediacaran (0.58 Ga) Doushantuo kerogen is similar to the O isotope composition previously obtained for the Silurian Zdanow kerogen of  $15.3 \pm 1.2\text{‰}$  (Tartèse *et al.*, 2016). For Bitter Springs kerogens, the  $\delta^{18}\text{O}$  values obtained by SIMS ( $8.6 \pm 3.7\text{‰}$ ) and by pyrolysis ( $17.3 \pm 0.6\text{‰}$  and  $17.5 \pm 0.6\text{‰}$ ) on kerogen residues isolated from two different samples are not consistent with each other. This may indicate that these two Bitter Springs samples correspond to slightly different time periods and/or deposition environments, for example, which can only be thoroughly assessed with further petro-geochemical investigation.



**Figure 1** (a) Oxygen isotope compositions of the kerogens analysed by SIMS and by pyrolysis plotted against their C isotope compositions. (b) Frequency distribution of the measured kerogen  $\delta^{18}\text{O}$  values.

The SIMS  $\delta^{18}\text{O}$  values for individual kerogens vary by  $\sim 10\text{--}15\text{‰}$  at the 20–30  $\mu\text{m}$  spot scale (Fig. S-1 and Table S-2). This variability, and the variations of the measured C, O, S and Fe intensities (Fig. S-2), are similar to the variability observed for Phanerozoic kerogens (Tartèse *et al.*, 2016). It is also comparable with the variations of 5–10‰ observed at the micrometre scale for C isotope ratios in Precambrian microfossils (*e.g.*, Williford *et al.*, 2013). For each sample, individual  $\delta^{18}\text{O}$  values display unimodal Gaussian distributions around their mean value (Fig. S-1), showing that there is no analytical evidence for multiple organic O-bearing components with variable O isotope compositions in the kerogens. The good consistency between combustion and SIMS average  $\delta^{18}\text{O}$  values obtained on selected samples (Table 1) indicates that most of the SIMS  $\delta^{18}\text{O}$  variability at the sample scale can be assigned to analytical effects (*e.g.*, sample topography, sputtering of mineral micro-inclusions; see Supplementary Information). This allows us to use both bulk kerogen pyrolysis and average SIMS  $\delta^{18}\text{O}_{\text{kerogen}}$  values (and their standard deviation) to estimate the O isotope composition of water coeval with the kerogen precursor biomass.

The last point to consider is the possible effects of diagenesis and metamorphism on preservation of the  $\delta^{18}\text{O}_{\text{kerogen}}$  values through time. During heating, kerogen loses O (and other heteroatoms such as N) as  $\text{H}_2\text{O}$ , CO and  $\text{CO}_2$ , which could in theory lead to enrichment in  $^{18}\text{O}$  in the residual kerogen due to preferential loss of molecules containing light  $^{16}\text{O}$ . The bulk kerogens analysed by Wedeking (1983) are up to *ca.* 3.5 billion years old and have large ranges of H/C ratios (from 0.1 to 1.4) and O contents (0.3–18.4 wt. %) (Table S-1). In these samples,  $\delta^{18}\text{O}_{\text{kerogen}}$  values are neither correlated with O contents nor with H/C ratios (Fig. S-3). Therefore, there is no evidence that  $\delta^{18}\text{O}$  values measured in the majority of the kerogens have been significantly altered during diagenesis and low grade metamorphism. As indicated previously, analysis of three recent



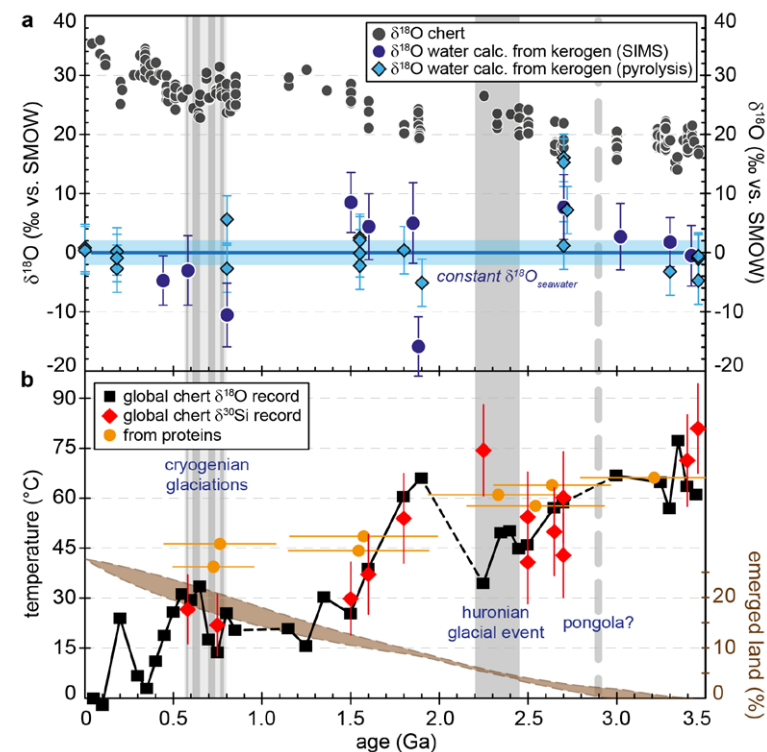
kerogens yielded a  $\Delta^{18}\text{O}_{\text{kerogen-water}}$  of  $20.5 \pm 1.1\text{‰}$  (Wedeking, 1983). The possible effect of temperature on biochemical O isotope fractionation is uncertain and debated (e.g., Roden and Ehleringer, 2000; Sternberg and Ellsworth, 2011), and this could introduce an additional uncertainty of ca.  $\pm 2\text{--}3\text{‰}$  on the O isotope composition of OM precursors. Therefore, we used a  $\Delta^{18}\text{O}_{\text{kerogen-water}}$  of  $20 \pm 4\text{‰}$  to calculate  $\delta^{18}\text{O}_{\text{water}}$  from kerogen O isotope compositions.

**Table 1** Main characteristics of the studied samples.  $\delta^{13}\text{C}$  and the  $\delta^{18}\text{O}$  values are given relative to VPDB and SMOW, respectively. See Supplementary Information for details and references.

Sample	Reference	Age (Ga)	Location	$\delta^{18}\text{O}_{\text{SIMS}}$ (‰)	$\delta^{18}\text{O}_{\text{TC/EA-IRMS}}$ (‰)	$\delta^{13}\text{C}$ (‰)
Doushantuo	1a of 8/25/83	0.58	Doushantuo Fm., Yangtze Gorges, South China	$17.0 \pm 4.3$	$15.0 \pm 0.1$	-29.9
Bitter Springs	3 of 11/2/90	0.80	Bitter Springs Fm., Amadeus Basin, Australia	$8.6 \pm 3.7$	–	-27.0
Jixian	1 of 8/14/83	1.50	Gaoyuzhuang Group, Jixian section, North China Block, China	$28.5 \pm 3.1$	–	-31.4
McArthur	7 of 6/21/90	1.60	McArthur Basin, Northern Territory, Australia	$24.4 \pm 3.9$	–	-25.1
Nabberu	PPRG 089	1.85	Top of Frere Fm., Earahedy Group, Nabberu Basin, Western Australia	$25.0 \pm 5.5$	–	-29.0
Gunflint	3 of 6/30/84	1.88	Schreiber Beach, Gunflint Iron Fm., Ontario, Canada	$4.4 \pm 2.2$	$7.3 \pm 0.5$	-34.5
	PPRG 134			$4.1 \pm 3.4$	–	-33.5
Wabigoon	PPRG 325	2.70	Steep Rock Group, Wabigoon Belt, Western Superior Province, Canada	$27.7 \pm 3.7$	–	-31.3
Farrel Quartzite	MGTKS1	3.02	Mount Grant, Gorge Creek Group, Pilbara Craton, Australia	$22.7 \pm 3.9$	$19.8 \pm 0.1$	-33.2
Josefsdal	99SA07	3.30	Top of Kromberg Fm., Onverwacht Group, Barberton Greenstone Belt, South Africa	$21.8 \pm 1.1$	–	-26.8
Buck Reef	99SA03	3.42	Base of Kromberg Fm., Onverwacht Group, Barberton Greenstone Belt, South Africa	$19.5 \pm 3.2$	$15.0 \pm 0.4$	-24.8

## Oxygen Isotope Composition of Water Derived from Kerogens

For most samples the calculated  $\delta^{18}\text{O}_{\text{water}}$  are consistent within errors with a value around  $0 \pm 2\text{‰}$  (Fig. 2a). Overall, the O isotope composition of water reconstructed from the O isotope composition of kerogens up to ca. 3.5 Ga is, therefore, indistinguishable from that of present-day seawater. This is consistent

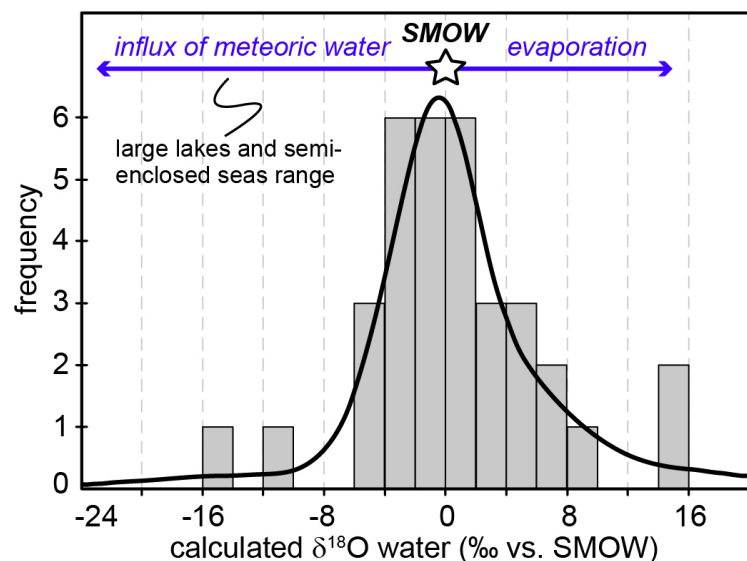


**Figure 2** (a) Comparison of the chert and calculated seawater O isotope composition evolution through time, calculated using a  $\Delta^{18}\text{O}_{\text{kerogen-water}}$  of  $20 \pm 4\text{‰}$ . Errors bars correspond to the propagated uncertainties on calculated  $\delta^{18}\text{O}_{\text{water}}$  (including the standard deviation – 1 SD – on average kerogen  $\delta^{18}\text{O}$  values and the uncertainty of  $\pm 4\text{‰}$  on  $\Delta^{18}\text{O}_{\text{kerogen-water}}$ ). The horizontal blue band represents a constant  $\delta^{18}\text{O}_{\text{seawater}}$  of  $0 \pm 2\text{‰}$  through time. (b) Estimates of water  $T$  calculated using (i) the available maximum  $\delta^{18}\text{O}_{\text{chert}}$  value (to which 3‰ has been added to take into account possible effects induced by diagenesis – see Supplementary Information) per 50 Ma age intervals and using  $\delta^{18}\text{O}_{\text{seawater}} = 0 \pm 2\text{‰}$ , (ii) the chert  $\delta^{30}\text{Si}$  record (Robert and Chaussidon, 2006) and (iii) resurrected proteins of ancient bacteria (Gaucher *et al.*, 2008). Estimates of the surface of emerged land through time are also shown (Flament *et al.*, 2013). Vertical grey bars running across both panels correspond to the major glaciation events identified in the geological record (after Hambrey and Harland, 1985; Evans *et al.*, 1997 and Young, 2014).



with inferences made from the study of seawater-altered Precambrian oceanic crust remnants (*e.g.*, Lécuyer and Allemand, 1999; Pope *et al.*, 2012), but does not support a *ca.* 10-15‰ progressive increase of  $\delta^{18}\text{O}_{\text{seawater}}$  since 3.5 Ga (Kasting *et al.*, 2006; Jaffrés *et al.*, 2007).

Kerogens from the 1.88 Ga Gunflint Formation collected at Schreiber Beach yielded low  $\delta^{18}\text{O}$  values of *ca.* 4‰, corresponding to a  $\delta^{18}\text{O}_{\text{water}}$  of around -15‰ (Fig. 3). A possible interpretation is that this low  $\delta^{18}\text{O}_{\text{water}}$  corresponds to cold shallow waters with a restricted connection with the open ocean and affected by a large influx of low  $\delta^{18}\text{O}$  continental waters, similar to the present-day Baltic Sea, for example ( $\delta^{18}\text{O}_{\text{water}}$  of -4 to -8‰; Jasechko *et al.*, 2013). This hypothesis would imply that the Gunflint cherts formed at low  $T < 10^\circ\text{C}$ , which is not incompatible with the palaeolatitude of *ca.* 45°N estimated for that region at 1.88 Ga (see Supplementary Information). On the other hand, kerogens from the 2.7 Ga Belingwe (Manjeri Fm.) and Ventersdorp samples yielded elevated  $\delta^{18}\text{O}$  values of *ca.* 35‰, corresponding to  $\delta^{18}\text{O}_{\text{water}}$  of ~-15‰ (Fig. 3). A possible interpretation is that precursor OM of these kerogens thrived in warm waters undergoing intense evaporation, which is consistent with the continental depositional environments proposed for these formations (Buck, 1980; Hunter *et al.*, 1998).



**Figure 3**  $\text{O}$  isotope composition of waters in which precursor biomass of the studied kerogens lived. SMOW corresponds to the present-day mean seawater composition. The range of  $\delta^{18}\text{O}$  values for large lakes and semi-enclosed seas is after Jasechko *et al.* (2013).

## Implications for Surface Temperatures on the Earth during the Precambrian

A globally constant  $\delta^{18}\text{O}_{\text{seawater}}$  around  $0 \pm 5\text{‰}$  through time, as demonstrated by the present results, implies that Precambrian cherts record formation  $T$  decreasing from 50-60°C during the Archean to 0-15°C for the recent Phanerozoic (Fig. 2b). For some Precambrian formations these elevated precipitation  $T$  may reflect mixing of seawater with hot hydrothermal fluids (*e.g.*, de Wit and Furnes, 2016). Also, some chert units may have been deposited in environments disconnected from the global oceans. However, taken as a whole the secular decrease of the  $\delta^{18}\text{O}_{\text{chert}}$  record, constructed from 569 individual  $\delta^{18}\text{O}_{\text{chert}}$  analyses representing a worldwide sampling, indicates a global cooling of the conditions on the Earth surface over geological time (Fig. 2b). This is consistent with other estimates such as the temperature of stability measured for resurrected proteins presumably akin those of Precambrian bacteria (Gaucher *et al.*, 2008; Fig. 2b). Elevated  $T$  around 35-50°C at 2.2-2.5 Ga appear in conflict with the existence of widespread cold surface conditions during the 'Huronian Glacial Event'. However, there is still no definitive proof supporting a worldwide extent for Huronian glaciations (Young, 2014). Also, global glacial episodes are relatively short (few hundred thousand to a few million years; Prave *et al.*, 2016) so a set of Precambrian chert samples, which are often poorly dated, defining the  $\delta^{18}\text{O}_{\text{chert}}$  for a given 50 Ma time interval, may not have formed contemporaneously with a known glacial period. Finally, it is important to note that reconstructed  $T$  have remained below *ca.* 30°C for the past 1.5 Ga, well within the range allowing development of complex eukaryotic life (*e.g.*, Clarke, 2014).

Elevated surface  $T$  of ~40-60°C during Archean times, when the Sun was 20-25% fainter than today (Gough, 1981), required an effective greenhouse atmosphere that may have been controlled by high pressures of  $\text{CO}_2$  ( $P_{\text{CO}_2}$ ) and of  $\text{CH}_4$  ( $P_{\text{CH}_4}$ ) (*e.g.*, Kasting and Ono, 2006). Recent 3D Global Climate Model simulations yielded average surface  $T$  of ~20°C around 3.4 Ga for  $P_{\text{CO}_2}$  and  $P_{\text{CH}_4}$  of 0.1 bar and 2 mbar, respectively (Charnay *et al.*, 2013). Further simulations also show that higher mean surface  $T$  (up to *ca.* 50°C) can be obtained by combining  $P_{\text{N}_2}$  and  $P_{\text{CO}_2}$  of 0.5 bar (Supplementary Information). Such atmospheric pressures are not in contradiction with measurements of  $\text{N}_2^{36}\text{Ar}$  in Archean hydrothermal fluids (Marty *et al.*, 2013) and studies of fossil imprints of 2.7 Ga rain droplets (Som *et al.*, 2012), which suggest maximum  $P_{\text{N}_2} = 1.1$  bar and  $P_{\text{CO}_2} = 0.7$  bar around 3.0-3.5 Ga (Marty *et al.*, 2013). Finally, the progressive decrease of surface  $T$  reconstructed from the chert record is inversely correlated with progressive emerging of the continents since *ca.* 3.0 Ga (Fig. 2b). This relationship suggests that the first order control on Earth surface  $T$  at a geological time scale is the consumption and sequestration of atmospheric  $\text{CO}_2$  by weathering of silicates on continental surfaces followed by carbonate deposition (*e.g.*, Berner *et al.*, 1983).



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## Additional Information

**Supplementary Information** accompanies this letter at [www.geochemicalperspectivesletters.org/article1706](http://www.geochemicalperspectivesletters.org/article1706)

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