

A palaeotemperature curve for the Precambrian oceans based on silicon isotopes in cherts

François Robert¹ & Marc Chaussidon²

The terrestrial sediment record indicates that the Earth's climate varied drastically in the Precambrian era (before 550 million years ago), ranging from surface temperatures similar to or higher than today's to global glaciation events¹. The most continuous record of sea surface temperatures of that time has been derived from variations in oxygen isotope ratios of cherts (siliceous sediments)², but the long-term cooling of the oceans inferred from those data^{3–5} has been questioned because the oxygen isotope signature could have been reset through the exchange with hydrothermal fluids after deposition of the sediments⁶. Here we show that the silicon isotopic composition of cherts more than 550 million years old shows systematic variations with age that support the earlier conclusion of long-term ocean cooling and exclude post-depositional exchange as the main source of the isotopic variations. In agreement with other lines of evidence^{1,7}, a model of the silicon cycle in the Precambrian era shows that the observed silicon isotope variations imply seawater temperature changes from about 70 °C 3,500 million years ago to about 20 °C 800 million years ago.

We selected a suite of chert samples that covers most of the available sedimentary record from the early Archaean era (3.5 Gyr ago) to the present (see Methods). Our sample set includes 9 Phanerozoic samples and 99 Precambrian samples dating from about 3.5 Gyr ago to about 0.5 Gyr ago and coming from 23 geological formations (Supplementary Table S1). These cherts were selected on the basis of several criteria ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values⁸) that were indicative of good preservation of their original structure and composition (some of them have been extensively studied for their abundant microfossils⁹). The O and Si isotopic composition were measured with a multicollector Cameca IMS 1270 ion microprobe (see Methods).

The $\delta^{18}\text{O}$ values of cherts show large variations that, for a given geological age, range from the maximum previously determined by Knauth and Lowe³ (hereafter reported as $\delta^{18}\text{O}_{\text{KL}}$) down to $\delta^{18}\text{O} = \delta^{18}\text{O}_{\text{KL}} - 15\text{‰}$ (Fig. 1). The curve defined by the maximum $\delta^{18}\text{O}$ ($\delta^{18}\text{O}_{\text{KL}}$) for a given age was proposed to reflect formation temperatures at depth in the sediment. These formation temperatures are in turn related to past seawater temperatures (Fig. 1). The oxygen isotopic fractionation between chert and water ($\Delta^{18}\text{O} = \delta^{18}\text{O}_{\text{chert}} - \delta^{18}\text{O}_{\text{water}}$) depends on temperature according to the equation $1,000\ln(\Delta^{18}\text{O}) = (3.09 \times 10^6 T^{-2}) - 3.29$. The large range in $\delta^{18}\text{O}$ indicates that a significant fraction of Precambrian cherts had their original $\delta^{18}\text{O}$ values lowered by post-depositional isotopic exchange with meteoric or hydrothermal fluids³ or, in some cases, were formed over a large range of temperature⁵.

The $\delta^{30}\text{Si}$ values of the present Phanerozoic cherts (nine samples) vary from $-1.7 \pm 0.8\text{‰}$ to $+1.3 \pm 0.3\text{‰}$ (1 s.d.) (see Supplementary Table S1), covering the range previously determined for diatoms collected from open ocean surface waters (from $+0.9\text{‰}$ to $+1.9\text{‰}$)¹⁰, diatoms from sedimentary cores ($+1.3\text{‰}$ to $+1.6\text{‰}$)¹¹

or siliceous sediments from black smokers (-3.5‰ to -0.2‰)^{12,13}. In contrast, the present set of Precambrian cherts shows much higher $\delta^{30}\text{Si}$ values (ranging from $-1.1 \pm 0.4\text{‰}$ to $+5.0 \pm 0.8\text{‰}$; Supplementary Table S1). Such high $\delta^{30}\text{Si}$ values have no counterpart in the Phanerozoic sedimentary record but were previously reported for a few Precambrian stromatolitic cherts^{12,13}. Detailed studies of Onverwacht cherts⁴ or of modern deep-sea cherts¹⁴ have shown that their $\delta^{18}\text{O}$ values can depart from equilibrium with sea water by up to about -10‰ ⁵ because of either the contribution of meteoric waters to the diagenetic fluids or the range in the crystallization temperatures during burial diagenesis. To account in our data set for this oxygen isotopic variability inherent in the process of chert formation, we tentatively consider here that cherts having $\delta^{18}\text{O} \leq \delta^{18}\text{O}_{\text{KL}} - 6\text{‰}$ did not preserve an original isotopic oceanic signature. Using this criterion, it turns out that all the cherts (56 out of 99) having $\delta^{18}\text{O}_{\text{KL}} - 6\text{‰} \leq \delta^{18}\text{O} \leq \delta^{18}\text{O}_{\text{KL}}$ show both an increase in their $\delta^{30}\text{Si}$ values with time from 3.5 to 0.8 Gyr (Fig. 2a) when they return abruptly to modern values and a corresponding positive correlation between their $\delta^{30}\text{Si}$ and $\delta^{18}\text{O}$ values (Fig. 2b). Note that using a

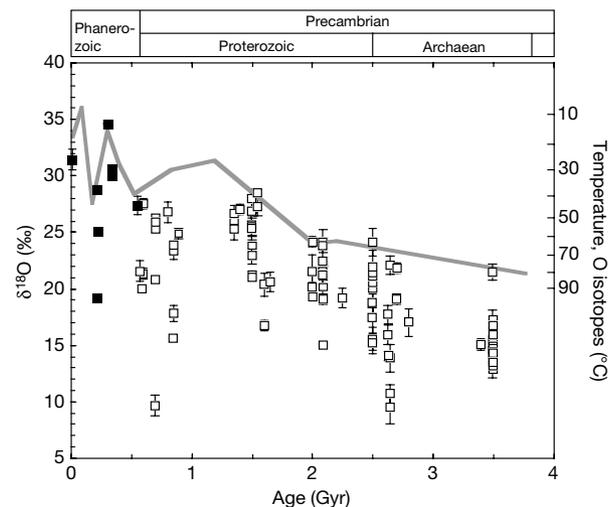


Figure 1 | Variation in chert $\delta^{18}\text{O}$ values with geological age. Open squares, our Precambrian samples; filled squares, Phanerozoic samples. Error bars correspond to 1σ error on the mean of three to five analyses per sample. The solid line (referred to in the text as $\delta^{18}\text{O}_{\text{KL}}$ (ref. 3)), shows the highest $\delta^{18}\text{O}$ value found in cherts at a given age. Considering that the ice caps were absent—that is, $\delta^{18}\text{O}_{\text{sea water}} = -1\text{‰}$ —variation in $\delta^{18}\text{O}_{\text{KL}}$ with time may reflect seawater temperature variations³ between about 70 °C in the early Archaean and about 30 °C in the late Proterozoic. $\delta^{18}\text{O}$ values of modern deep-sea cherts¹⁴ can depart from equilibrium with sea water by up to about -4‰ (see the text). These variations, which are inherent in the process of chert crystallization, control the precision on seawater temperature.

¹Muséum National d'Histoire Naturelle, CNRS LEME NanoAnalyses, UMS 2679, 57 rue Cuvier, 75005 Paris, France. ²Centre de Recherches Pétrographiques et Géochimiques, CRPG-CNRS BP20, 54501 Vandœuvre-lès-Nancy, France.

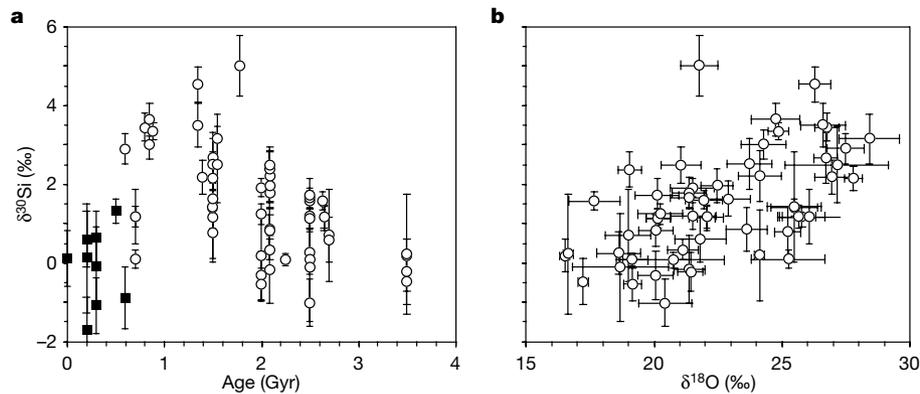


Figure 2 | Variation of $\delta^{30}\text{Si}$ with $\delta^{18}\text{O}$ values and geological age for samples with the highest $\delta^{18}\text{O}$ values. The highest $\delta^{18}\text{O}$ values for a given age are defined by $\delta^{18}\text{O}_{\text{KL}} - 6\permil < \delta^{18}\text{O} < \delta^{18}\text{O}_{\text{KL}}$, see text. Error bars for $\delta^{18}\text{O}$ and $\delta^{30}\text{Si}$ values correspond to 1σ error on the mean of three to five analyses per sample. Precambrian cherts (open circles) have $\delta^{30}\text{Si}$ values

threshold of $4\permil$ ($\delta^{18}\text{O}_{\text{KL}} - 4\permil \leq \delta^{18}\text{O} \leq \delta^{18}\text{O}_{\text{KL}}$) restricts the number of chert samples to 40 out of 99 but does not change the correlations observed in Fig. 2. The positive correlation between $\delta^{30}\text{Si}$ and $\delta^{18}\text{O}$ vanishes for cherts with $\delta^{18}\text{O} < \delta^{18}\text{O}_{\text{KL}} - 6\permil$ (Fig. 3). Thus, the threshold at about $6\permil$ on $\delta^{18}\text{O}$ values seems a relevant criterion to distinguish between samples with different O–Si isotopic systematics.

The $\delta^{30}\text{Si}$ – $\delta^{18}\text{O}$ correlation (Fig. 2b) seems hardly compatible with post-depositional isotopic exchange with hydrothermal fluids, which would have lowered both $\delta^{18}\text{O}$ and $\delta^{30}\text{Si}$. If a low temperature (about 15°C) is assumed for the Precambrian oceans, cherts must form with $\delta^{18}\text{O} = +32\permil$ and, to fit the correlation reported in Fig. 2, with a $\delta^{30}\text{Si}$ of between $+6\permil$ and $+8\permil$. In addition, samples with $\delta^{18}\text{O} < \delta^{18}\text{O}_{\text{KL}} - 6\permil$, for instance Rietgat samples (Supplementary Table S1), show that the $\delta^{30}\text{Si}$ values remain essentially unchanged whereas $\delta^{18}\text{O}$ is reset through the interaction with high-temperature fluids (Fig. 3). This behaviour is qualitatively in agreement with the fact that, as Si is insoluble in fluids, the water/rock ratios for the two isotopic systems are quite different.

In contrast with oxygen isotopes, there is apparently no significant temperature effect on the Si isotopic fractionation between precipi-

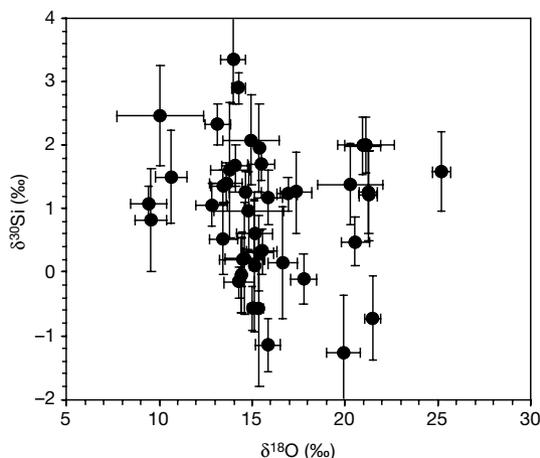


Figure 3 | Variations of $\delta^{30}\text{Si}$ with $\delta^{18}\text{O}$ values for samples with low $\delta^{18}\text{O}$ values ($\delta^{18}\text{O} < \delta^{18}\text{O}_{\text{KL}} - 6\permil$). Error bars for $\delta^{18}\text{O}$ and $\delta^{30}\text{Si}$ values correspond to 1σ error on the mean of three to five analyses per sample. The lack of correlation between $\delta^{18}\text{O}$ and $\delta^{30}\text{Si}$ values for these samples shows that the decrease in $\delta^{18}\text{O}$ values (by up to $15\permil$), probably caused by the interaction with high-temperature fluids, has a limited effect on the $\delta^{30}\text{Si}$ values.

much higher than those of Phanerozoic ones (filled squares). The change in $\delta^{30}\text{Si}$ values is sharp at the end of the Precambrian. In addition, the $\delta^{30}\text{Si}$ values increase during the Precambrian (a), which parallels the $\delta^{18}\text{O}$ evolution, resulting in a positive correlation between $\delta^{30}\text{Si}$ and $\delta^{18}\text{O}$ values (b).

tated and dissolved silicon^{12,15,16}. Thus, variations of chert $\delta^{30}\text{Si}$ values must primarily reflect variations in the $\delta^{30}\text{Si}$ of the fluids from which they formed.

The major difference in the marine silica cycle between the Phanerozoic¹⁷ and the Precambrian¹⁸ is the rapid development about 0.6 Gyr ago of organisms that used dissolved silicon to build their skeleton: biogenic silica precipitation maintains the Si concentration in sea water today at $[\text{Si}]_{\text{sw}} \approx 4.5 \text{ p.p.m.}$ ¹⁷. In contrast, in the Precambrian $[\text{Si}]_{\text{sw}}$ was probably controlled by both the solubility of amorphous silica, which resulted in a much higher $[\text{Si}]_{\text{sw}}$ than today (for example 49 p.p.m. at 20°C (ref. 21)), and the rate of silicification of the oceanic crust¹⁸. This major difference has profound consequences for the $\delta^{30}\text{Si}$ value of Precambrian oceans and for its evolution with time.

In the absence of biogenic precipitation of silica—that is, during the Precambrian—it can be considered that seawater Si had two major outputs: the sedimentary silica precipitated from pore sea water and the hydrothermal silica resulting from the silicification of the oceanic crust. The sedimentary silica was transformed into cherts during diagenesis, process that we consider to be at the origin of our chert samples with $\delta^{18}\text{O} \leq \delta^{18}\text{O}_{\text{KL}} - 6\permil$. At steady state, isotopic mass balance must be fulfilled between the input and output Si fluxes. This Si budget can be written in a manner similar to that formulated, for instance, for the oceanic carbon isotopic budget, which is controlled by the relative outputs of carbonates and reduced carbon and the isotopic fractionation between the two carbon pools. For Si, the budget should be controlled by the relative outputs of sedimentary and hydrothermal silica and the associated isotopic fractionations (see Supplementary Fig. S2) so that

$$\delta^{30}\text{Si}_{\text{In}} = f\delta^{30}\text{Si}_{\text{Sed}} + (1-f)\delta^{30}\text{Si}_{\text{Hyd}}$$

where $\delta^{30}\text{Si}_{\text{In}}$ is the isotopic composition of the Si input (input includes contributions from mantle and continental crust) to the marine cycle, f is the relative fraction of sedimentary Si precipitated from sea water or pore sea water in sediments (subscript Sed) and $(1-f)$ is the counterpart retrieved by the hydrothermal silicification of the crust (subscript Hyd). The major Si isotopic fractionation in this system (defined as $\Delta^{30}\text{Si}_{\text{Hyd-In}} = \delta^{30}\text{Si}_{\text{Hyd}} - \delta^{30}\text{Si}_{\text{In}}$) is predicted to have taken place during the silicification of the crust. Although not yet studied experimentally, a negative value seems likely for $\Delta^{30}\text{Si}_{\text{Hyd-In}}$: first, $\delta^{30}\text{Si}$ values down to $-3.5\permil$ (ref. 13) have been reported for siliceous sediments precipitated at black smokers from hydrothermal fluids with $\delta^{30}\text{Si} = -0.3\permil$ (ref. 11) and second, isotopic fractionations between precipitated silica and dissolved silicon are observed to be of the order of $-1\permil$ (refs 12, 15, 16). In addition,

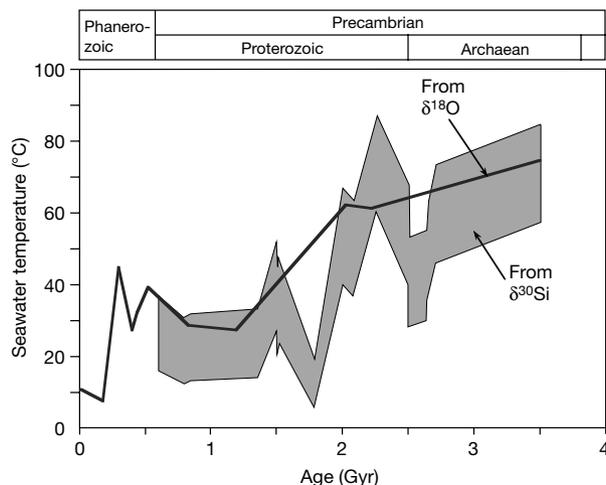


Figure 4 | Variations in oceanic temperatures modelled from the $\delta^{30}\text{Si}$ values from cherts (grey area) compared with the curve proposed from $\delta^{18}\text{O}$ values³. The silicon isotope thermometer has been calculated on the assumption that either the maximum temperature (at 3.5 Gyr ago) or the minimum temperature (at 0.8 Gyr ago) indicated by the $\delta^{18}\text{O}$ values is correct (see Supplementary Information). Although the global significance of the silicon isotope temperature curve can be questioned at certain geological times (namely, apparent strong cooling at about 1.8 and about 2.5 Gyr ago) as a result of limited sampling, the $\delta^{30}\text{Si}$ values from the cherts are consistent with a significant decrease in oceanic temperatures since 3.5 Gyr ago, in agreement with results from oxygen isotopes.

if the silicification process involves the diffusion of Si, then kinetic isotopic effects can be predicted that would enrich the hydrothermally deposited silica in ^{28}Si . Because the exact value of $\Delta^{30}\text{Si}_{\text{Hyd-In}}$ is unknown, we considered it to be a free parameter calculated by the model. Numerical calculations (detailed in the Supplementary Information) show that it varies between about -1% and about -3% ; that is, within a range that agrees with theoretical expectations. It is obvious from the mass balance equation that, for negative $\Delta^{30}\text{Si}_{\text{Hyd-In}}$ values, $\delta^{30}\text{Si}_{\text{Sed}}$ is positive and increases when f decreases. This is in qualitative agreement with the positive $\delta^{30}\text{Si}$ found in the present cherts.

Furthermore it seems that the regular increase in chert $\delta^{30}\text{Si}$ values during the Precambrian (Fig. 2a) can be used as a ‘palaeothermometer’ for sea water: this comes from the fact that seawater temperature (T_{sw}) is the major control on f .

Consider that the Si concentration in the hydrothermal fluids circulating in the silicified crust is at equilibrium with quartz at the fluid temperature (T_{Hyd}), whereas sea water is in equilibrium with amorphous silica at T_{sw} . When hydrothermal fluids percolating the oceanic crust return to the surface, they have to cool and to equilibrate with sea water (or with pore sea water). Because the solubility of quartz in hydrothermal fluids¹⁹ at temperatures for which the precipitation rate of silica is maximal²⁰, $T > 190^\circ\text{C}$ (see Supplementary Information), is higher than that of amorphous silica²¹ for any realistic seawater temperature (that is, $T < 70^\circ\text{C}$), these fluids lose a large fraction of their Si on the way to the surface. This fraction, referred to as $(1-f)$ in the mass balance equation, depends on the difference between T_{Hyd} and T_{sw} , which implies that ultimately it depends on T_{sw} : if T_{sw} decreases, the amount of Si sequestered by silicification of the crust increases (that is, f decreases) and thus $\delta^{30}\text{Si}_{\text{Sed}}$ increases.

This process holds only if part of the silicon injected into seawater precipitates as amorphous silica. This would occur systematically if dissolved silicon in sea water were at, or slightly above, the saturation level relative to amorphous silica (see Supplementary Information) as postulated for the Proterozoic¹⁸. After the appearance of Si-fixing organisms, presumably in the early Phanerozoic, it can be supposed that, as today, sea water was always maintained strongly undersaturated relative to amorphous silica. In this situation, hydrothermal

fluids that are discharged into sea water cool and are diluted, always remaining undersaturated relative to amorphous silica. In our model, this would correspond to $f = 0$, in agreement with the rather constant and low (close to mantle) $\delta^{30}\text{Si}$ values found for Phanerozoic cherts (Fig. 2a).

As detailed numerically in Supplementary Information, this approach allows us to calculate—from the $\delta^{30}\text{Si}$ –age relationship defined by Precambrian cherts—a relationship between T_{sw} and age. For this calculation, the $\delta^{30}\text{Si}$ values of the chert samples with $\delta^{18}\text{O} \leq \delta^{18}\text{O}_{\text{KL}} - 6\%$ have been averaged for each geological formation (Supplementary Table S2). The $\delta^{30}\text{Si}$ of the input flux was taken to be -0.3% ; this is the value of the mantle and of the fluids at black smokers^{11,22}; that is, the value of the mantle input to the sea–water–crust system. Continental clay formation and silicification processes^{23,24} that could have changed the $\delta^{30}\text{Si}$ value of the riverine input are ignored in this model. They could not account for the $\delta^{30}\text{Si}$ – $\delta^{18}\text{O}$ correlation (Fig. 2b) because the $\delta^{18}\text{O}$ value of the oceans in the Precambrian was not controlled by continental erosion.

Taking 70 and 30°C , given by $\delta^{18}\text{O}_{\text{KL}}$, for seawater temperatures at 3.5 and 0.85 Gyr, respectively, allows us to solve the mass balance equation for a range of $\Delta^{30}\text{Si}_{\text{Hyd-In}}$ and T_{Hyd} (see Supplementary Information for details). The corresponding range of possible T_{sw} values for the Precambrian is indicated by the grey region in Fig. 4. The calculated trend of decreasing T_{sw} during the Precambrian is then in striking agreement with that predicted previously from O isotopes. This approach also predicts the positive correlation observed in cherts between $\delta^{18}\text{O}$ and $\delta^{30}\text{Si}$. Thus, O and Si isotopic compositions of cherts concur to show that large changes in surface temperature occurred during the Precambrian.

METHODS

Geological formations (location, geology and radiometric ages) of all the samples studied here are reviewed in refs 9, 25. Specific information on aliquots of the samples studied can be found in refs 25–28. The other samples come from three different collections: first, the Caltech collection (courtesy of P. Knauth and S. Epstein; referred to in Supplementary Table S1 as K for Knauth samples; previous isotopic studies of some of the samples studied can be found in refs 2, 3, 29); second, the samples collected by S. Awramik (courtesy of S. Awramik; referred to as ‘n of month–day–year’ of the recovery); and third, the Precambrian Palaeobiology Research Group collection referred to as PPRG (courtesy of J. W. Schopf)²⁵.

The sample fragments were embedded in epoxy (about ten in each mount), coated with gold and sputtered with a Cs^+ primary beam (5–10 nA intensity and about $30\ \mu\text{m}$ in size) and the electron gun. The negative $^{16}\text{O}^-$, $^{18}\text{O}^-$, $^{28}\text{Si}^-$ and $^{30}\text{Si}^-$ ions produced during sputtering were accelerated at 10 kV and analysed at a mass resolution $M/\Delta M$ of about 3,000 in multi-collection mode by using Faraday cups (O and Si isotopic ratios were measured in different sessions; see recent developments of these techniques^{23,30}). We used quartz standards (Rose quartz and NBS-28) and an internal chert standard (miocene chert from the Paris basin) that was systematically included in all the mounts and analysed together with the samples. For Si, we assumed that there was no matrix effect on instrumental mass fractionation between chert and quartz.

$\delta^{30}\text{Si}$ and $\delta^{18}\text{O}$ are expressed relative to the NBS-28 and Vienna standard mean ocean water (VSMOW) international standards, respectively; for example $\delta^{30}\text{Si} = 1,000 \times [({}^{30}\text{Si}/{}^{28}\text{Si})/({}^{30}\text{Si}/{}^{28}\text{Si})_{\text{NBS}} - 1]$ and similarly for $\delta^{18}\text{O}$.

During the different analytical sessions in which the two quartz standards were run together, the Rose quartz standard gave $\delta^{30}\text{Si}$ values relative to NBS-28 of $+0.24 \pm 0.14\%$, $+0.20 \pm 0.20\%$, $+0.16 \pm 0.40\%$ and $+0.34 \pm 0.40\%$. The precision of the $\delta^{18}\text{O}$ and $\delta^{30}\text{Si}$ measurements was not limited by counting statistics (about $\pm 0.1\%$ and $\pm 0.05\%$, respectively) but probably by sample heterogeneity: our internal chert standard (Miocene chert) gave $\delta^{18}\text{O}$ and $\delta^{30}\text{Si}$ values ranging within $\pm 0.49\%$ (1σ , 53 analyses) and $\pm 0.28\%$ (1σ , 48 analyses), respectively. Between three and five analytical spots were made systematically on each sample to document the possible isotopic variability on a small scale (for example, analysis of silica veins cross-cutting the silica ground mass were avoided). When available, the bulk $\delta^{18}\text{O}$ values of some samples—previously determined at the milligram scale by the classical BrF_5 oxidation procedure^{2,3,29}—were compared with the values obtained by the ion probe at the nanogram scale: both sets of data agreed within $\pm 1.9\%$ on average (Supplementary Fig. S1). This rather large scatter illustrates the fact that, in some rare cases, oxygen isotopic heterogeneity up to $+3.3\%$ (sample K500 in

Supplementary Table S1) are present at the millimetre scale. The data (reported in Supplementary Table S1) are averages over the different analytical spots made on a given sample. The 1σ error (from $\pm 0.2\text{‰}$ to $\pm 2.3\text{‰}$ for $\delta^{18}\text{O}$ and from $\pm 0.25\text{‰}$ to $\pm 1.4\text{‰}$ for $\delta^{30}\text{Si}$) on these averages reflects the isotopic variability within a given sample.

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Supplementary Information is linked to the online version of the paper at www.nature.com/nature.

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Author Contributions Both authors contributed equally to this work.

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