

PALAEOCLIMATOLOGY

Evidence for hot early oceans?

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The oxygen isotopes in sedimentary cherts (siliceous sediments) have been used to argue that the Precambrian oceans were hot — with temperatures of up to 70 °C at 3.3 Gyr before present¹. Robert and Chaussidon² measure silicon isotopes in cherts and arrive at a similar conclusion. We suggest here that both isotope trends may be caused by variations in seawater isotope composition, rather than in ocean temperatures. If so, then the climate of the early Earth may have been temperate, as it is today, and therefore more consistent with evidence for Precambrian glaciations and with constraints inferred from biological evolution.

By focusing on cherts, Robert and Chaussidon² have overlooked the much more extensive marine-carbonate oxygen-isotope database³. Marine carbonates can be more easily demonstrated by using strontium isotopes^{3,4}, for example, to relate to the global ocean, whereas two different mineralogies — dolomite [CaMg(CO₃)₂] and calcite (CaCO₃) — are studied in parallel. According to the oxygen- and silicon-isotope data of Robert and Chaussidon², surface seawater temperatures decreased by 50–60 °C during the Precambrian, mostly between 2.0 Gyr and 1.0 Gyr ago. Such a major change in ocean temperature ought to be recorded in the marine carbonate record by a rise in $\delta^{18}\text{O}$ values of at least 10‰: however, no such rise is evident.

If only the average values of each unit are plotted (to reduce bias from individual studies with many samples), then a much smaller (~5‰) rise in carbonate $\delta^{18}\text{O}$ is seen between 2.5 Gyr and 0.8 Gyr ago³. This rise could represent a much more modest temperature decrease of about 20 °C, which would be more consistent with evidence for glaciation and from fossil and biomarker records of eukaryo-

tes throughout this period in Earth's history.

On the other hand, secular changes in marine chert and carbonate $\delta^{18}\text{O}$ values, and perhaps $\delta^{30}\text{Si}$ values as well, need have nothing to do with temperature. The largest shift in carbonate $\delta^{18}\text{O}$ occurred more recently during the early Palaeozoic⁴ and has been interpreted as resulting mainly from an increase in seawater $\delta^{18}\text{O}$ (see refs 4, 5, for example). This is because of the implausibly hot global climate that would need to be inferred were temperature the sole controlling factor on carbonate $\delta^{18}\text{O}$ during this period of animal expansion.

The secular change in $\delta^{18}\text{O}$ of cherts can also be explained if seawater isotopic composition changes with time^{6,7}. This possibility, much discussed in the literature, has been overlooked by Robert and Chaussidon². If the increase in marine chert and carbonate $\delta^{18}\text{O}$ from the Archaean to the present day were caused by an equivalent increase in seawater $\delta^{18}\text{O}$, then it must have been related to a decrease in the relative influence of low- versus high-temperature alteration of the ocean crust^{5–7}. Such a decrease could have been caused by changes in tectonic styles associated with decreasing geothermal heat flow^{7,8}. In particular, if the mid-ocean ridge crests were shallower in the past, hydrothermal circulation systems may have penetrated less deeply, and sea water may have interacted with basalts at lower temperatures⁸.

Such a change in mid-ocean-ridge circulation systems may also explain the trend towards higher seawater $\delta^{30}\text{Si}$ during the Precambrian noted by Robert and Chaussidon². In their model, the silicon isotope composition of sea water is controlled by the fraction of silica that leaves the ocean in sediments, f , compared with the fraction, $1 - f$, that leaves as a result of hydrothermal silicification of oceanic crust. The

latter fraction, $1 - f$, depends on the temperature difference between the circulating hydrothermal fluid, T_{hyd} , and sea water, T_{SW} . The smaller the difference between these two numbers, $T_{\text{hyd}} - T_{\text{SW}}$, the smaller is the fraction $1 - f$ and the greater is the fraction f . The authors' data² show that the early Precambrian was characterized by a greater value of f , or a smaller value of $1 - f$, which they interpret as indicating an increase in T_{SW} . The implicit assumption here is that T_{hyd} remains constant. We propose that this change might equally well be caused by a decrease in T_{hyd} , while T_{SW} remains more or less constant. Such a model, driven by changes in heat flow and plate tectonics⁸, offers a natural explanation for the secular changes in both $\delta^{18}\text{O}$ and $\delta^{30}\text{Si}$ in sedimentary rocks — one that does not conflict with the observed record of Precambrian glaciations and biological evolution.

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Robert & Chaussidon reply

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The possibility of a change in $\delta^{18}\text{O}$ values of the oceans has been discussed for the past 30 years¹ and the comment by Shields and Kasting² does not really bring any new insight into this issue. The carbonate $\delta^{18}\text{O}$ curve³ is indistinguishable from that of cherts and shows a huge scatter caused by local geological processes. This scatter in $\delta^{18}\text{O}$ (up to 20‰ at a given age) far exceeds the sensitivity of the isotope thermometer (about 2‰ per 10 °C). It therefore prevents any precise additional test of the model and no consensus was ever reached

in the literature on this debate from oxygen-isotope data alone. Our approach⁴, by contrast, was to try to find another isotopic proxy ($\delta^{30}\text{Si}$) that could bring new and independent constraints to test the hypothesis of hot oceans in the early Precambrian. Our interpretation of the $\delta^{30}\text{Si}$ values in terms of temperature is fully coherent not only with the $\delta^{18}\text{O}$ of cherts but also with that of marine carbonates, and certainly does not overlook these data. In addition, we indicated⁴ that our sample set has not the time resolution that would be necessary

to look for an effect on silicon isotopes of Precambrian global glaciations. No chert samples from such periods were analysed.

A change in the $\delta^{18}\text{O}$ of sea water down to –15‰ (as indicated by the difference between modern and the Archaean chert values) that would result from a drastic change with time of the hydrothermal circulation at oceanic ridges would seem to be unattainable because there is no mineral assemblage that can fractionate oxygen isotopes to the extent required by models involving alteration of the oceanic crust^{5,6}.

In addition, the $\delta^{18}\text{O}$ values of mineral pairs in cherts (phosphate–silica)⁷ used to calculate the seawater $\delta^{18}\text{O}$ independently never give a $\delta^{18}\text{O}$ in sea water that departs by more than 5‰ (in both directions) from the present-day value.

Shields and Kasting² suggest that in our model⁴ a variation of the temperature of the hydrothermal fluids circulating in the oceanic crust, T_{hyd} , could be responsible for the change in $\delta^{30}\text{Si}$, instead of a variation in the seawater temperature. In our model, T_{hyd} varies between 190 and 230 °C. This range stands for the range of temperature at which most silica precipitation occurs from a fluid injected into the crust at about 300 °C. First-order calculations show that this T_{hyd} in the Archaean should be close to 110 °C in order to reproduce the $\delta^{30}\text{Si}$ variations observed in our data, with a constant seawater temperature of 10 °C.

How is it possible to lower T_{hyd} by about

100 °C while the Precambrian crust temperature was probably higher than the present-day value? Can such low-temperature fluids efficiently leach silicon in the oceanic crust and precipitate it to produce the silicon isotopic fractionation required to explain the chert data? Is it possible to obtain an equilibrium between dissolved and precipitated silica at such a low temperature, and at what rate? Although these issues cannot be simply addressed from existing experimental data or theoretical considerations, they might nevertheless be tested in cherts with the ion microprobe by quantifying the isotope homogeneity at the micrometre scale. Oxygen and silicon isotope studies of hydrothermal silica (silica veins in Precambrian rocks) should constrain the temperature of hydrothermal reactions and the isotopic composition of the fluids.

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