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► **To cite this version:**

Haoxuan Sun, Marc Chaussidon, François Robert, Shengyu Tian, Zhengbin Deng, et al.. Triple silicon isotope insights into the formation of Precambrian cherts. *Earth and Planetary Science Letters*, 2023, 607, pp.118069. 10.1016/j.epsl.2023.118069 . hal-04616152

HAL Id: hal-04616152

<https://hal.science/hal-04616152>

Submitted on 18 Jun 2024

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Triple silicon isotope insights into the formation of Precambrian cherts

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Abstract

Cherts are pervasive in the Precambrian and their O and Si isotopic compositions have been used extensively for reconstructing seawater paleo-temperatures. However, these reconstructions are obscured by the fact that cherts exhibit, at a given age, a large isotopic (O and Si) heterogeneity at bulk and micrometer scales. This is understood as reflecting the fact that cherts are an assemblage of silica precursors having different origins, and that diagenesis and metamorphism have modified the isotopic compositions acquired during the last equilibration with seawater. To test the contributions of the different processes that control the Si isotopic composition of cherts, we developed high-precision triple Si isotope measurements by Multicollector-Inductively Coupled-Plasma Mass-Spectrometer (MC-ICP-MS). This approach allows to identify deviations from the equilibrium Si isotopic fractionation at the level of a few ppm. Triple Si isotope data combined with trace elements and O isotope data in Precambrian cherts demonstrate that three different sources of silica were involved in the formation of cherts, and that both equilibrium and kinetic isotopic fractionation took place for Si. Archean seawater is predicted to have a triple Si isotopic composition kinetically fractionated relative to bulk silicate Earth. This requires a large kinetic isotopic fractionation during hydrothermalism of the oceanic crust and appears consistent with warm oceans in the Precambrian. However more work is required on the triple isotope systematics of Si inputs and output to seawater by rivers and authigenic clays formation. Triple Si isotope variations can thus be used as a new tool to unravel the origin of cherts and of their O and Si isotopic compositions. The present evidence of kinetic isotopic fractionations for Si isotopes also implies that Si isotopes should be associated to triple O isotope for paleotemperature reconstructions.

Keywords

Triple silicon isotope, kinetic isotopic fractionation, Precambrian chert, seawater temperature.

31 1. Introduction

32 Precambrian cherts are sedimentary rocks composed mainly of microquartz (i.e., micrometer size quartz
33 grains) formed during the diagenetic transformation of sediments rich in amorphous silica and precipitated on the
34 seafloor from seawater (Knauth, 2018). Before the evolution of silica-secreting organisms ~ 500 Ma, seawater was
35 presumably silica-saturated and cherts were consequently abundant among Precambrian marine sediments (Siever,
36 1992). The oxygen and silicon isotopic composition of cherts constitutes one of the major proxies to reconstruct the
37 evolution of seawater temperature in the Precambrian (Knauth and Lowe, 1978; Robert and Chaussidon, 2006).
38 Precambrian cherts have been shown to display secular systematic mass-dependent variations of oxygen and silicon
39 isotopes ($\delta^{18}\text{O}$ and $\delta^{30}\text{Si}$, see section 2) with, notably, a depletion of the heavier isotopes of oxygen and silicon in
40 Archean cherts (Knauth and Lowe, 1978; Robert and Chaussidon, 2006). The ~ 15‰ lower $\delta^{18}\text{O}$ values of early
41 Archean cherts relative to modern ones have been proposed to reflect seawater temperatures higher by ~ 55 - 85°C
42 (Knauth, 2005 and refs therein). Similarly, the ~ 4‰ $\delta^{30}\text{Si}$ variations, positively correlated with variations of $\delta^{18}\text{O}$
43 values, have been shown to be consistent with a change of ~ 50°C of seawater temperature (Robert and Chaussidon,
44 2006). In this model, the increase of seawater $\delta^{30}\text{Si}$ during the Archean results from an increase of the difference
45 between the temperature of hydrothermal fluids leaching the oceanic crust and that of seawater, causing an
46 increase of sequestration of hydrothermal quartz (depleted in ^{30}Si) in the oceanic crust and consequently an increase
47 of the $\delta^{30}\text{Si}$ brought to seawater by hydrothermal fluids.

48 However, a decrease of seawater temperature during the Archean is not the only process which can
49 contribute to the observed increase of seawater $\delta^{30}\text{Si}$. Si isotopic studies of rivers have shown that dissolved Si
50 released from the weathering of the continents has in average positive $\delta^{30}\text{Si}$ (from 0.2 to 1.5‰ with Yangtze River
51 extremely fractionated up to 3‰; De La Rocha et al., 2000; Ding et al., 2004; Gaspard et al., 2021; Georg et al., 2006).
52 This is due to the fact that ^{30}Si is enriched in water during the formation of secondary minerals such as clays and
53 during the uptake of Si by plants (De La Rocha et al., 1997; Opfergelt et al., 2008; Sun et al., 2016). While in
54 Phanerozoic times the Si flux to the oceans from the continents dominated over the hydrothermal flux from the
55 oceanic crust (Tréguer et al., 2021), this would have been very different in the early Archean. An increase of
56 continental versus hydrothermal sources, due to continental growth in the Archean, can contribute to the increase
57 of seawater $\delta^{30}\text{Si}$ (Chakrabarti et al., 2012). Another process able to affect the $\delta^{30}\text{Si}$ of seawater is the formation of
58 authigenic clays in marine sediments from cations dissolved in pore waters and seawater (or pore waters) Si, i.e.
59 reverse weathering (Trower and Fischer, 2019). While precipitation of amorphous silica from seawater will tend to
60 decrease, by mass balance, seawater $\delta^{30}\text{Si}$ (because amorphous silica is likely enriched in ^{30}Si , [Appendix](#)), the
61 formation of authigenic clays will deplete seawater in ^{30}Si (Oelze et al., 2015; Zheng et al., 2016). An increased flux
62 of Si sequestration by formation of authigenic clays relative to amorphous silica would result in an increased
63 seawater $\delta^{30}\text{Si}$ (Trower and Fischer, 2019).

64 Another limitation of temperature reconstructions based on O and Si isotopes is that they depend on two
65 critical assumptions. First, for reconstructions based on oxygen isotopes, the Precambrian seawater $\delta^{18}\text{O}$ must be
66 assumed. Several studies have shown that the $\delta^{18}\text{O}$ of seawater was constant at a time scale of 200 - 300 Ma and
67 close to its modern value (Gregory, 2003; Muehlenbachs and Clayton, 1976; Pope et al., 2012; Tartèse et al., 2017;
68 Olson et al., 2022) but this has been challenged by advocating that a secular change took place in the balance
69 between low-temperature and high-temperature fluid/rock interactions in the continental and oceanic crusts
70 (Herwartz, 2021; Jaffrés et al., 2007; Sengupta and Pack, 2018). Second, it must be assumed that the isotope
71 composition of the chert is controlled by isotopic equilibrium with seawater and has not been modified by secondary
72 processes such as hydrothermalism, metamorphism or alteration (Sharp et al., 2016). The validity of this assumption
73 is difficult to test because petrological observations (Knauth, 2018) and in-situ $\delta^{18}\text{O}$ and $\delta^{30}\text{Si}$ analyses (Marin et al.,
74 2010; Marin-Carbonne et al., 2012) have shown that cherts are actually very complex sedimentary rocks made
75 dominantly of microquartz, but containing also a significant fraction of other forms of silica. Microquartz itself is not
76 a direct precipitate from seawater but results from diagenetic transformations of the sedimentary amorphous silica
77 precursors, at temperatures higher than seawater and with pore fluids that can differ from seawater. Ion microprobe
78 $\delta^{18}\text{O}$ and $\delta^{30}\text{Si}$ analyses have shown that microquartz is characterized by several permil O and Si isotopic variations
79 at micrometer scale which reflect the process of diagenesis and can be used to quantify the degree of the
80 preservation of cherts (Marin-Carbonne et al., 2014 and refs therein). Back-correcting the effects of diagenesis on
81 the O isotopic composition, allows to better constrain the temperature of seawater with, for instance at 1.9 Ga from
82 microquartz in Gunflint cherts, 30 - 52°C (Marin et al., 2010), i.e. ~ 15 - 20°C lower than that calculated from bulk
83 $\delta^{18}\text{O}$ values on apparently pure microquartz fractions (Winter and Knauth, 1992).

84 Recently, improvements in the precision of oxygen isotopic measurements have demonstrated the
85 potential of triple oxygen isotope data in hydrothermal and sedimentary rocks to estimate both the temperature
86 and isotopic composition of the fluid with which the rock last equilibrated (Herwartz et al., 2015; Pack and Herwartz,
87 2014; Sharp et al., 2016). Triple oxygen isotope studies of Precambrian cherts still come to different conclusions on
88 Precambrian seawater temperatures with either values at around 70 °C (Lowe et al., 2020; McGunnigle et al., 2022)
89 or lower temperatures (Herwartz, 2021). Here we report the first high-precision triple silicon isotopic composition
90 of Precambrian cherts, including a suite of samples from a single ~ 1.5 Ga basin (Jixian cherts) and several Archean
91 cherts between 2.0 and 3.5 Ga. These data demonstrate that the silicon isotopic composition of the various forms
92 of quartz in Archean cherts is the result of a combination of equilibrium and kinetic isotopic fractionations. This
93 brings new constraints on the formation of Archean cherts and on the origin of the secular variations of their Si
94 isotopic composition and has also key potential consequences for seawater temperature reconstruction from O
95 isotopic compositions.

96 **2. Triple silicon isotope systematics**

97 The Si isotopic composition is traditionally reported in delta (δ) notation, which is the per mil deviation from
 98 the isotopic ratio of a reference standard:

$$\delta^i\text{Si} = \left[\left(\frac{{}^i\text{Si}/{}^{28}\text{Si}}{\text{sample}} / \left(\frac{{}^i\text{Si}/{}^{28}\text{Si}}{\text{standard}} \right) - 1 \right] \times 1000 \quad (1)$$

99 where i is the nucleon number of silicon isotopes (29 or 30) and NBS-28 (NIST[®]RM-8546) is used as the reference
 100 standard for Si isotopes. The isotopic fractionation factor (α) between phases A and B is defined as the ratio of the
 101 isotopic ratios in the two phases A and B:

$$\alpha_{A-B}^i = \left(\frac{{}^i\text{Si}/{}^{28}\text{Si}}{\text{A}} \right) / \left(\frac{{}^i\text{Si}/{}^{28}\text{Si}}{\text{B}} \right) \quad (2)$$

102 For an isotopic system with more than one isotopic ratio like silicon, the theory of mass-dependent isotopic
 103 fractionation shows that, at first order, fractionation factors are exponentially related:

$$\theta = \ln(\alpha_{A-B}^{29/28}) / \ln(\alpha_{A-B}^{30/28}) \quad (3)$$

104 where θ is the fractionation exponent and depends on the atomic masses of isotopes (e.g., Bigeleisen and Mayer,
 105 1947). θ is not a constant (e.g., Young et al., 2022), but its value is always close to the ratio of mass differences
 106 among isotopes, i.e., $\theta_{\text{Si}} \approx 0.5$. Consequently, in a 3-isotope diagram ($\delta^{30}\text{Si}$ versus $\delta^{29}\text{Si}$), the isotopic mass-dependent
 107 fractionation will approximately follow a straight line with a slope λ of ≈ 0.5 :

$$\lim_{\delta \rightarrow 0} \theta \approx \lim_{\delta \rightarrow 0} \frac{\delta^{29}\text{Si}_A - \delta^{29}\text{Si}_B}{\delta^{30}\text{Si}_A - \delta^{30}\text{Si}_B} \quad (4)$$

108 However, with improved analytical precision, the facts that θ varies in different processes (equilibrium and
 109 kinetic isotopic fractionations) and that the correlation between $\delta^{29}\text{Si}$ and $\delta^{30}\text{Si}$ is non-linear (Eq 4) make the bias
 110 from the real fractionation line in a 3-isotope diagram non-negligible anymore. Hulston and Thode (1965) firstly
 111 recast δ into a logarithmic form notation, delta prime (δ'), to remove this bias:

$$\delta'^i\text{Si} = \ln \left[\left(\frac{{}^i\text{Si}/{}^{28}\text{Si}}{\text{sample}} / \left(\frac{{}^i\text{Si}/{}^{28}\text{Si}}{\text{standard}} \right) \right] \times 1000 \quad (5)$$

112 and a strict linear relationship can be built by using delta prime notation (Miller, 2002):

$$\delta'^{29}\text{Si} = \lambda \times \delta'^{30}\text{Si} + \gamma \quad (6)$$

113 In the following we use delta prime notation for triple silicon systematics to avoid potential bias, even if this bias
 114 would be at the ppm level and, thus, negligible for the present Si isotopic variations in Precambrian cherts.

115 At high temperature, where the quantum effects are small (Bigeleisen and Mayer, 1947; Young et al., 2002),
 116 the maximum value of the equilibrium isotopic fractionation exponent, $\theta_{\text{eq,max}}$, can be simply calculated by:

$$\theta_{\text{eq,max}} = (1/m_{28} - 1/m_{29}) / (1/m_{28} - 1/m_{30}) \quad (7)$$

117 Substituting the mass (${}^{28}\text{Si}$: 27.97692649 \pm 0.00000022; ${}^{29}\text{Si}$: 28.97649468 \pm 0.00000022; ${}^{30}\text{Si}$: 29.97377018 \pm
 118 0.00000022; (Audi and Wapstra, 1993)) into Eq. 7 gives a value of $\theta_{\text{eq,max}} = 0.5178$. In the case of triple oxygen
 119 isotopes, which have been much more studied than triple silicon isotopes, it has been shown that θ_{eq} between
 120 quartz and water varies significantly with temperature, decreasing from 0.5305 ($\theta_{\text{eq,max}}$) to a minimum of 0.5237 at
 121 0°C (Sharp et al., 2016). No such study yet exists for triple silicon isotopes but it can be anticipated that the change

122 of θ_{eq} with temperature will be very small for silicon isotopes because the change of equilibrium $\alpha_{silica-water}$ with
 123 temperature is one order of magnitude smaller for Si isotopes (≈ 1 ‰ for the $^{30}\text{Si}/^{28}\text{Si}$ ratio between 25 and 75 °C,
 124 [Appendix](#)) than for O isotopes (≈ 11 ‰ for the $^{18}\text{O}/^{16}\text{O}$ ratio between 25 and 75°C, e.g. Sharp et al., 2016). The kinetic
 125 fractionation exponent, θ_k , can be estimated at first order by using Graham's law (Young et al., 2002):

$$\theta_k = \ln(m_{28}/m_{29}) / \ln(m_{28}/m_{30}) \quad (8)$$

126 giving a value of $\theta_k = 0.5092$, but complex kinetic fractionations in nature could have different θ_k .

127 With high precision triple Si isotope measurement, potential deviations from a given mass-dependent
 128 fractionation line can be observed in the $\delta^{129}\text{Si}$ - $\delta^{130}\text{Si}$ diagram. In general, these deviations could result either from
 129 nucleosynthetic anomalies and are usually noted $\epsilon^{129}\text{Si}$ for Si isotope data on meteorites (e.g., Pringle et al., 2013),
 130 or from variations of θ values resulting from complex mass-dependent isotopic fractionations, as it is the case
 131 potentially for Precambrian cherts. Thus, we prefer in the following to use the notation $\Delta^{129}\text{Si}$, as done for triple
 132 oxygen isotopes in cherts. The value of $\Delta^{129}\text{Si}$ (or of $\epsilon^{129}\text{Si}$) expressed in ppm is given by:

$$\epsilon^{129}\text{Si} \text{ or } \Delta^{129}\text{Si} = (\delta^{129}\text{Si} - 0.5178 \times \delta^{130}\text{Si}) \times 1000 \quad (9)$$

133

134 3. Materials and methods

135 Based on previous developments of Si isotopic analysis by MC-ICP-MS at IPGP (Paris, France) (Deng et al.,
 136 2019; Pringle et al., 2014), we improved the technique for triple Si isotopes by, specifically, reducing potential
 137 isobaric interferences on Si isotopes ([Appendix](#)). This technique returns $2\sigma_{SE}$ for $\Delta^{129}\text{Si}$ between 3 to 8 ppm. This
 138 precision is sufficient to detect whether Si isotopes are fractionated by equilibrium ($\theta_{eq} = 0.5178$) or kinetic ($\theta_k =$
 139 0.5092) processes in case of $\delta^{130}\text{Si}$ variations ≥ 0.5 ‰ (a variation of $\Delta^{129}\text{Si}$ by 8.6 ppm is predicted for a 1‰
 140 fractionation of $\delta^{130}\text{Si}$ by a kinetic process). In addition to Si isotopic compositions, $\delta^{18}\text{O}$ compositions of the cherts
 141 that were not available from previous studies were measured by ion microprobe (MC-SIMS) at CRPG-CNRS (Nancy,
 142 France) using standard procedures previously described (Marin et al., 2010; Robert and Chaussidon, 2006). The
 143 major and minor element contents were measured by ICP-MS at IPGP after acid digestion of the same powders of
 144 samples that were used for the triple Si isotopic measurements ([Appendix](#)).

145 Cherts were collected by S.M. Awramick and the Precambrian Paleobiology Research Group (PPRG, Schopf
 146 and Klein, 1992), including one Neoproterozoic chert (Bitter Springs Fm., 0.8 Ga), eight Mesoproterozoic cherts
 147 (Jixian section, 1.35 - 1.50 Ga), two Paleoproterozoic cherts (Gunflint Fm., 2.0 Ga) and five Archean cherts (Tumbiana
 148 Fm., Onverwacht Grp., Warrawoona Grp., 2.72-3.50 Ga). These samples have been previously studied for their $\delta^{18}\text{O}$
 149 and $\delta^{30}\text{Si}$ (Marin et al., 2010; Marin-Carbonne et al., 2012; Robert and Chaussidon, 2006) and their geological settings
 150 have been described ([Appendix](#)). The eight Jixian samples were chosen to study in more details the origin of possible
 151 Si isotopic variations within a given Proterozoic sedimentary basin which contains thick layers of interbedded
 152 carbonates and cherts that were sedimented after a rifting event at 1.6 Ga (Li et al., 2013).

153 4. Results

154 All the cherts, by definition, contain mostly silica, but non-siliceous veins and inclusions are frequently
155 observed. Chert fragments devoid of veins and inclusions were carefully handpicked for analysis. However, while
156 most cherts have bulk SiO₂ contents > 90 wt%, two samples (Jixian 8 of 8/18/83 and Jixian 8/18/83, Table S2) have
157 lower SiO₂ contents due to the presence of high contents of either Al₂O₃ and K₂O (6.34 wt% Al₂O₃ and 8.01 wt% K₂O
158 for Jixian 8 of 8/18/83). Otherwise, all cherts have low and variable contents of minor elements with no significant
159 differences between the Jixian suite (0.03 - 1.31 wt% CaO, 0.05 - 0.90 wt% MgO, 0.01 - 1.02 wt% FeO), the 2.09 Ga
160 Gunflint samples (0.05 - 1.50 wt% CaO, 0.06 - 0.73 wt% MgO, 0.88 - 1.17 wt% FeO, 0.09 - 0.31 wt% Al₂O₃, consistent
161 with previous ion probe data in Marin-Carbonne et al., 2012), and the Archean cherts (\leq 0.45 wt% CaO, \leq 0.16 wt%
162 MgO, 0.13 - 0.87 wt% FeO, 0.14 - 1.14 wt% Al₂O₃, consistent with the compositions previously reported, Hofmann et
163 al., 2013; Sugitani, 1992; Sugitani et al., 2006). Note also that variations in Al₂O₃, TiO₂, K₂O and Zr are often positively
164 correlated. The $\delta^{18}\text{O}$ values measured for the Jixian cherts range from 23.1‰ to 29.3‰, which is within the ranges
165 previously found (e.g., 10.09 - 28.43‰ in (Robert and Chaussidon, 2006), 15.7-27.8‰ in (Ding et al., 2017)). All the
166 $\delta^{18}\text{O}$ values of the present cherts are consistent with the general trend of decreasing $\delta^{18}\text{O}$ values with age established
167 by (Fig. 1A, Knauth and Lowe, 1978).

168 The present cherts show a large range of variations for $\delta^{30}\text{Si}$ values from $-1.139 \pm 0.025\text{‰}$ to $2.925 \pm$
169 0.014‰ , Neoproterozoic and Mesoproterozoic cherts having more positive $\delta^{30}\text{Si}$ values than Paleoproterozoic ones
170 (Table 1, Fig. 1B). This range of variations and this systematics are consistent with previous *in situ* data (Robert and
171 Chaussidon, 2006; Sengupta and Pack, 2018; Tartèse et al., 2017) and bulk data (Chakrabarti et al., 2012; Ding et al.,
172 2017). The present data confirm the large range ($\sim 3\text{‰}$, from 0.170 to 2.925‰) of $\delta^{30}\text{Si}$ values for Jixian cherts,
173 previously observed with *in situ* data (0.76 - 4.53‰, Robert and Chaussidon, 2006) and bulk data (0.5 - 3.9‰, Ding
174 et al., 2017). Overall, there is a clear positive correlation between the present bulk $\delta^{30}\text{Si}$ values and the previous ion
175 probe $\delta^{30}\text{Si}$ data, however with some scatter (Fig. S3). This is likely due to the fact that the ion probe data were
176 collected only in microquartz while the present bulk $\delta^{30}\text{Si}$ data are an average of the different forms of silica in the
177 cherts (microquartz, veins of hydrothermal quartz, detrital quartz grains) which have been shown by ion probe to
178 have potentially different $\delta^{30}\text{Si}$ values in a given chert (Marin-Carbonne et al., 2012). The present bulk $\delta^{30}\text{Si}$ values
179 show a broad positive trend with the microquartz $\delta^{18}\text{O}$ values (Fig. S8), as observed previously between $\delta^{30}\text{Si}$ and
180 $\delta^{18}\text{O}$ values on microquartz (Robert and Chaussidon, 2006), suggesting that the bulk $\delta^{30}\text{Si}$ values are primarily
181 controlled by the composition of the microquartz.

182 A significant range of $\Delta^{29}\text{Si}$ values, from -20 ± 4 to 28 ± 4 ($2\sigma_{\text{SE}}$), is observed in the present cherts (Table 1).
183 This could not be detected previously given the lower precision of published data (Pringle et al., 2014). In the triple
184 Si isotopes diagram ($\delta^{29}\text{Si}$ - $\delta^{30}\text{Si}$), the Jixian samples plot between the theoretical equilibrium and the kinetic mass-
185 dependent fractionation lines assumed to cross at the Si isotopic composition of mantle basalts as represented by
186 the BHVO-2 standard ($\delta^{30}\text{Si} = -0.31\text{‰}$ and $\delta^{29}\text{Si} = -0.16\text{‰}$, Pringle et al., 2014) and define a slope of 0.5123 ± 0.0022

187 ($2\sigma_{SE}$). In a $\Delta^{129}\text{Si}-\delta^{130}\text{Si}$ diagram this gives a slope of -5.51 ± 2.16 ($2\sigma_{SE}$) between the equilibrium and kinetic mass
188 fractionation lines (Fig. 3A). There is no clear trend of $\Delta^{129}\text{Si}$ values with age (Fig. 1C), the most positive $\Delta^{129}\text{Si}$ are
189 present in the 3.5 Ga cherts ($\Delta^{129}\text{Si}$ values from 7 ± 8 to 28 ± 4 ppm) while the most negative $\Delta^{129}\text{Si}$ values are in the
190 Jixian cherts. The 3.5 Ga cherts do not plot on the $\Delta^{129}\text{Si}-\delta^{130}\text{Si}$ line defined by the Jixian cherts (Fig. 2).

191 5. Discussion

192 5.1 Three-endmember sources of SiO_2 in cherts

193 The systematic variations between the chemical compositions and the $\delta^{130}\text{Si}$ values of the present cherts
194 imply the existence of three sources for Si in cherts. The first one is detrital silica, clearly observed in cherts with high
195 Al_2O_3 contents (3.77 - 6.34 wt%). These cherts have $\delta^{130}\text{Si}$ values close to 0‰, as expected for detrital particulate
196 silica from the continents which is likely to have a $\delta^{130}\text{Si}$ close to that estimated for the bulk upper continental crust
197 (-0.25 ± 0.16 ‰, Savage et al., 2013). The positive trend between Al_2O_3 and K_2O contents (Fig. S5), regardless of chert
198 types and ages, points to the systematic presence in cherts of detrital materials from the continents (Marin-Carbonne
199 et al., 2012; Sugitani et al., 2002; Van den Boorn et al., 2010). Detrital silica would be characterized by high Al_2O_3
200 contents with a range of $\text{Al}_2\text{O}_3/\text{K}_2\text{O}$ ratios reflecting the compositional range of the continental source (Sugitani et
201 al., 2002). Because of the secular increase of the volume of continental crust, the fraction of detrital silica in cherts
202 has likely increased with time, which could explain why the highest fraction of detrital silica is observed in some
203 Jixian cherts. The two other sources of silica can be clearly identified in cherts with low Al_2O_3 content (< 0.48 wt%)
204 which have a range of $\delta^{130}\text{Si}$ values from 0.32 ± 0.04 ‰ to 2.93 ± 0.01 ‰ (Fig. 5A). A similar $\delta^{130}\text{Si}-\text{Al}_2\text{O}_3$ systematics
205 was observed in 3.5 Ga cherts from the Pilbara craton (Van den Boorn et al., 2010) and interpreted as reflecting the
206 presence in these cherts of (i) chemical precipitates (named C-cherts and Al_2O_3 -poor) from a mixture between
207 Archean seawater (positive $\delta^{130}\text{Si}$ values) and hydrothermal fluids (negative $\delta^{130}\text{Si}$ values) and of (ii) volcanic materials
208 silicified by seawater (Al_2O_3 -rich and slightly positive $\delta^{30}\text{Si}$ values).

209 As also previously observed (Van den Boorn et al., 2010), the presence in cherts of silica of various origins
210 is reflected in the variations of the cherts REE contents. This is observed for the present Jixian cherts where the ones
211 with high Al_2O_3 content have the highest total REE contents (39.29 - 84.50 ppm) and are enriched in LREE similarly
212 to the upper continental crust (PAAS, Taylor and McLennan, 1981). The cherts with low Al_2O_3 content have much
213 lower total REE contents with either a small positive Eu anomaly in agreement with a hydrothermal input (Van den
214 Boorn et al., 2010) or a strongly fractionated pattern possibly related to seawater (Fig. S7, Bolhar et al., 2004).

215 5.2 Signatures of kinetic and equilibrium processes in the silicon isotopic composition of cherts

216 The range in $\Delta^{129}\text{Si}$ values found for the present Precambrian cherts, distributing in a $\Delta^{129}\text{Si}$ versus $\delta^{130}\text{Si}$
217 diagram between the lines for $\theta_{eq,max}$ (0.5178) and for θ_k (0.5092), is strongly suggestive of the fact that Si in cherts
218 records both kinetic and equilibrium Si isotopic fractionations. Though θ_{eq} has not yet been determined for

219 temperatures in the range from 0 to 75°C, it seems likely, by analogy with triple O isotopes as explained in section 2,
220 that the effect of temperature cannot decrease θ_{eq} from 0.5178 to 0.5092. Similarly, θ_k might depart slightly from
221 0.5092 depending on the process fractionating Si, but no data exist to quantify this effect. In the following we
222 consider that these potential variations of θ_{eq} and θ_k are second order relative to the present large range found for
223 triple silicon isotopic compositions of cherts and we use as a first approach $\theta_{eq}=0.5178$ and the $\theta_k = 0.5092$.

224 Several equilibrium and kinetic Si isotopic fractionations during the marine Si cycle and the complex
225 formation of cherts can be expected.

226 (1) Considering, first, the direct precipitation of amorphous silica from seawater, the equilibrium
227 fractionation factor $1000 \ln \alpha_{silica-fluid}^{30} (= \delta^{130}Si_{silica} - \delta^{130}Si_{fluid},$ noted as $\Delta^{30}Si_{silica-fluid}$ in the following) seems to be too
228 small to produce the >3‰ variations of $\delta^{130}Si$ observed in Jixian cherts or Archean cherts. The most extreme values
229 for equilibrium $\Delta^{30}Si_{silica-fluid}$, determined theoretically or experimentally under different conditions, range from -2.1
230 to 2.1‰ ([Appendix](#)). Therefore, making a chert with $\delta^{130}Si$ of 3‰ from a fluid with dissolved silica having $\delta^{130}Si \approx -0.3‰$
231 (the value predicted for Archean seawater if dissolved silica derives predominantly from leaching of Si from the
232 oceanic crust, Siever, 1992) would require either to fractionate the fluid by an extreme reservoir effect with a
233 negative $\Delta^{30}Si_{silica-fluid}$ (for instance, the removal of ~90% of Si from the fluid with a $\Delta^{30}Si_{silica-fluid}$ of -2.1‰ would result
234 in a fractionated fluid with $\delta^{130}Si = -0.3 - 2.1 \times \ln(0.1) = 4.5‰$, from which precipitation of silica should take place and
235 get a $\delta^{130}Si$ of +2.4‰) or to have a very strong $\Delta^{30}Si_{silica-fluid}$ of >3.3‰, which seems unlikely since the most probable
236 values for equilibrium $\Delta^{30}Si_{silica-fluid}$ during precipitation of silica ranges from 0.1 to 1.6‰ for 25~75°C and pH 6~9
237 ([Appendix](#), note that we consider an average equilibrium $\Delta^{30}Si_{silica-fluid}$ of +0.8‰ in the following discussion). Thus,
238 larger Si isotopic fractionations of kinetic origin, either during the formation of cherts or in the marine cycle (i.e.
239 changing the Si isotopic composition of seawater) are required.

240 (2) The large $\Delta^{30}Si_{silica-fluid}$ determined in some hydrothermal systems (e.g. from -2.40 to -5.49‰ at Cistern
241 spring in Yellowstone national park, Chen et al., 2020, [Appendix](#)) shows that silica can be precipitated in such a
242 system with a large kinetic isotopic fractionation. This apparent isotopic fractionation is consistent with values
243 determined experimentally or theoretically (Oelze et al., 2014; Roerdink et al., 2015). Thus, by a reservoir effect,
244 large kinetic Si isotopic fractionations could be present in Si delivered to seawater by hydrothermal fluids leaching
245 the oceanic crust, as previously proposed to be one cause of increase of seawater $\delta^{30}Si$ in the Archean (Robert and
246 Chaussidon, 2006). Studies of the silica-water system in the range 0 – 300°C have shown that a hydrothermal fluid
247 ascending the crust and cooling rapidly will become supersaturated relative to solid silica species, leading to a rapid
248 increase in the rate of silica precipitation (Rimstidt and Barnes, 1980). Assuming a kinetic $\Delta^{30}Si_{silica-fluid} \approx -2.0‰$ (Oelze
249 et al., 2014) and $\theta_k = 0.5092$, the Si remaining in the fluid and delivered to the oceans would be isotopically
250 fractionated with $\delta^{130}Si$ and $\Delta^{129}Si$ values from 3.63 ‰ to 1.74 ‰ and from -34 to -18 ppm, respectively (Fig. 4). This
251 will also result in the presence on (or below) the seafloor of hydrothermal silica with strongly negative $\delta^{130}Si$ values

252 that can be remobilized during diagenesis for the formation of cherts. Amorphous silica precipitated from seawater
253 could thus have a Si isotopic composition reflecting both a source effect (kinetically fractionated hydrothermal Si
254 added to seawater) and the process of precipitation itself (at equilibrium with seawater).

255 (3) The growth of continents made rivers to become an important Si flux to seawater, presumably during
256 the late Archean. Even if there was no biogenic uptake of dissolved Si in rivers by plants in the Archean (one of the
257 major Si fractionation in soils waters today, e.g. Sun et al., 2016), it is reasonable to assume that dissolved Si in river
258 had an isotopic composition kinetically fractionated. First, the large fractionation in hot springs has been proven to
259 be kinetic as discussed above. Second, the flow-through experiment by Geilert et al 2014 suggests a kinetic
260 precipitation with $\Delta^{30}\text{Si}_{\text{silica-fluid}}$ from -2.1 to -0.5‰ at surface conditions and at temperatures of 10~40°C. Furthermore,
261 adsorption processes during the formation of secondary minerals are kinetic and have a $\Delta^{30}\text{Si}_{\text{solid-fluid}}$ between -1.5‰
262 and -3.3‰ (Oelze et al., 2015; Zheng et al., 2016). Thus, dissolved Si in late Archean rivers was probably kinetically
263 fractionated and enriched in heavy Si isotopes.

264 (4) Another process which has been proposed to control seawater Si isotope composition is the formation
265 of banded iron formations (BIF) and, in marine sediments, of authigenic clays. Modeling of the marine Si cycle in the
266 Precambrian has shown that the observed change of chert $\delta^{30}\text{Si}$ could be explained, dominantly, by a change in the
267 relative proportions of amorphous silica and authigenic clays formed, both phases removing Si from seawater and
268 pore waters (Trower and Fisher, 2019). Unfortunately, there is at present no Si isotope data that allow to constrain
269 precisely the Si isotopic fractionation that takes place during the formation of authigenic clays. In the following we
270 use the isotopic fractionation ($\delta^{30}\text{Si}$ of authigenic clays is 2‰ lower than that of amorphous silica) taken by Trower
271 and Fisher (2019) in their model. We consider that this fractionation is equilibrium and not kinetic, as it is the case
272 for amorphous silica precipitation, though this is clearly a point that must be studied in the future.

273 **5.3 Implications of triple silicon isotopes on the formation of the 1.5 Ga Jixian cherts**

274 The silicon isotopic variations ($\delta^{30}\text{Si}$ and $\Delta^{29}\text{Si}$) observed in the suite of Jixian cherts can be understood as
275 reflecting the presence of different silica components formed with different isotopic fractionation factors (Fig. 3C,
276 3D). In the following working model (Fig. 3), we try to explore, first, how the different major sources and sinks of
277 marine Si will control the Si isotope composition of amorphous silica in a $\Delta^{29}\text{Si}$ versus $\delta^{30}\text{Si}$ space, and then, how
278 the formation of cherts will modify the Si isotopic composition in this space.

279 We consider that during the Proterozoic, dissolved Si in seawater was (i) recharged by rivers and
280 hydrothermal fluids leaching the oceanic crust and (ii) extracted by the precipitation of amorphous silica and the
281 formation of authigenic clays. Assuming a temperature of seawater at 1.5 Ga \approx 40°C (Marin et al., 2010) and
282 hydrothermal fluids initially at 300°C at depth in the oceanic crust, 85% of dissolved silica in the hydrothermal fluids
283 would kinetically precipitate as hydrothermal quartz with average $\delta^{30}\text{Si}$ and $\Delta^{29}\text{Si}$ of -1.23‰ and 8 ppm, respectively.

284 Slightly warmer or cooler oceans would not modify the general relationship predicted between $\delta^{130}\text{Si}$ and $\Delta^{129}\text{Si}$ in
285 Fig. 3D and Fig. 4. Si remaining in the hydrothermal fluids is fractionated to $\delta^{130}\text{Si} = 2.47\text{‰}$ and $\Delta^{129}\text{Si} = -24$ ppm (Fig.
286 4), and mixed with dissolved Si from rivers. The flux and $\delta^{130}\text{Si}$ of rivers in Precambrian is not well constrained but
287 the Si isotopic composition can be assumed to be $\delta^{130}\text{Si} \approx 1\text{‰}$ (slightly lower than modern rivers due to the absence
288 of biogenic uptake of Si) and with a kinetic isotopic signature (see previous section) so that $\Delta^{129}\text{Si} \approx -11$ ppm.
289 Depending on the relative fluxes of hydrothermal Si and riverine Si, seawater would have a Si isotopic composition
290 in between these two endmembers (see Fig. 3D). Assuming a relative flux of Si uptake from seawater by formation
291 of authigenic clays and amorphous silica of 60% and 40%, respectively (Trower and Fischer, 2019) and isotopic
292 fractionations described in previous section, by mass balance, the seawater $\delta^{130}\text{Si}$ would be increased by 0.4‰
293 without change in $\Delta^{129}\text{Si}$ (Fig. 3D). Amorphous silica precipitated from seawater is thus expected to have a range in
294 Si isotopic composition with $\delta^{130}\text{Si}$ from 1.8 to 3.7 ‰ and $\Delta^{129}\text{Si}$ from -11 to -24 ppm (Fig. 3D).

295 Upon diagenesis, chert is formed with Si coming from amorphous silica, hydrothermal quartz and detrital
296 quartz. Because the Si isotopic composition of detrital silica from the continents ($\delta^{130}\text{Si} = -0.25 \pm 0.16$ ‰ and $\Delta^{129}\text{Si}$
297 assumed to be 0 ppm) plots in Fig. 3D nearly on the mixing line between hydrothermal silica and amorphous silica,
298 the presence of various proportions of these three components in the precursors of Jixian cherts results in the
299 negative linear trend observed for Jixian cherts (Fig. 3D), which is between theoretical equilibrium and kinetic
300 isotopic fractionation lines. Taking Al_2O_3 content as a proxy for the detrital input from the continents, the clear
301 systematics observed for Precambrian cherts between $\Delta^{129}\text{Si}$ values and Al_2O_3 contents (Fig. 5B) is consistent with
302 inferences made in section 5.1 from the systematics between $\delta^{130}\text{Si}$ values and Al_2O_3 contents. It can be explained
303 by a mixture among three types of silica: (i) a detrital end-member with high Al_2O_3 contents and with $\delta^{130}\text{Si}$ and $\Delta^{129}\text{Si}$
304 close to -0.25 ‰ and 0 ppm (not significantly fractionated relative to silicate Earth), (ii) amorphous silica precipitated
305 from seawater with low Al_2O_3 and fractionated Si isotope composition (positive $\delta^{130}\text{Si}$ and negative $\Delta^{129}\text{Si}$), and (iii)
306 hydrothermal silica with low Al_2O_3 and Si isotopic composition fractionated at the opposite than amorphous silica
307 (negative $\delta^{130}\text{Si}$ and positive $\Delta^{129}\text{Si}$). From their Al_2O_3 contents and $\delta^{130}\text{Si}$, we calculate that Jixian cherts contain from
308 27 to 89% (59% on average) of amorphous silica precursor, from 11 to 63% of hydrothermal silica precursor (36% on
309 average), and from 0.2 to 25% of detrital silica from the continents. At variance, note that most of the present > 2.0
310 Ga cherts have compositions closer to the hydrothermal end-member (62% on average, Fig. 5, Table S4), even taking
311 into account that Archean oceans might have been warmer than 40°C (see table S3).

312 **5.4 Triple Si isotopes evidences for diagenetic and metamorphic secondary processes in Archean cherts**

313 Triple Si isotopes appear key to test the presence of secondary isotopic fractionations (of O and Si) that
314 must be taken into account for reconstruction of seawater temperature. For instance, in a $\Delta^{129}\text{Si}$ - $\delta^{130}\text{Si}$ diagram, some
315 Archean cherts plot outside the field defined by the equilibrium and kinetic fractionation lines ($\Delta^{129}\text{Si} > 10$ ppm at
316 $\delta^{130}\text{Si}$ around $\sim 0\text{‰}$, Fig. 2). Such isotopic compositions cannot be produced by mixing hydrothermal and seawater
317 amorphous silica precursors fractionated from a fluid leaching the oceanic crust, even considering there was less or

318 no river flux (Fig. 3A, 3B) and whatever the temperatures considered for seawater. Note that the addition of
319 continental detrital Si does not move the Si isotopic composition of chert outside this field. Thus, the presence of
320 positive $\Delta^{129}\text{Si}$ for a $\delta^{130}\text{Si}$ close to 0‰ (as in most of the present Warrawoona and Onverwacht cherts) requires the
321 occurrence of processes resulting in additional Si isotopic fractionations. These processes remain yet unclear but the
322 fact that the highest $\Delta^{129}\text{Si}$ are associated to the lowest $\delta^{18}\text{O}$ values (from 13.6 to 15.4‰, Table 1, Fig. 2) indicates
323 the possibility of strong effects of diagenesis and metamorphism (Marin et al., 2010). An appropriate combination
324 of kinetic and equilibrium isotopic fractionations ($1/3 \times \text{kinetic} + 2/3 \times \text{equilibrium}$, Roerdink et al., 2015) during
325 dissolution and reprecipitation of SiO_2 at 150°C would for instance result in a slope of -0.43 in the $\Delta^{129}\text{Si}$ - $\delta^{130}\text{Si}$ diagram
326 (Fig. S6). This would allow to move the initial Si isotopic composition of a chert to the composition observed in some
327 of the present > 2.0 Ga cherts during several successive steps of dissolution/re-precipitation of silica. In such a
328 scenario, the original silica would have had a Si isotopic composition of $\delta^{130}\text{Si} \sim 0.76$ ‰ and $\Delta^{129}\text{Si} \sim -5$ ppm, such an
329 isotopic composition necessitating a seawater temperature at around 60°C (Fig. 3A, 3B). At variance, the five
330 fragments of the Tumbiana chert studied plot close to the hydrothermal end-member in the $\Delta^{129}\text{Si}$ - $\delta^{130}\text{Si}$ diagram
331 (Fig. 2), in agreement with previous inferences made from $\delta^{130}\text{Si}$ values and concentrations of Al_2O_3 , K_2O , TiO_2 and
332 FeO (Marin-Carbonne et al., 2012). Thus, a possible criterion to select Precambrian cherts for seawater temperature
333 reconstruction, in addition to the criteria described in (Marin-Carbonne et al., 2014), is that their Si isotopic
334 compositions remain between the equilibrium and kinetic lines in the $\Delta^{129}\text{Si}$ - $\delta^{130}\text{Si}$ diagram. In such samples (e.g.,
335 present Tumbiana and Gunflint samples), microquartz with high $\delta^{18}\text{O}$ is likely deriving from silica precipitated from
336 seawater.

337 5.5 Potential consequences for triple oxygen isotope systematic

338 The identification of kinetic isotopic fractionations for Si in cherts from their $\Delta^{129}\text{Si}$ - $\delta^{130}\text{Si}$ systematics has
339 potential consequences on the use of triple oxygen isotope compositions to reconstruct paleotemperatures. In the
340 $\Delta^{17}\text{O}$ - $\delta^{18}\text{O}$ diagram, many Precambrian cherts have triple oxygen isotopic compositions plotting to the left of the
341 curve calculated for equilibrium with ice-free seawater (Fig 6, Sharp et al., 2016). This shift can be explained by a
342 lower $\delta^{18}\text{O}$ for the Archean Ocean (Sengupta et al., 2020), the involvement of meteoric waters or hydrothermal
343 fluids during the formation of cherts, or secondary processes such as alteration and metamorphism (Abraham et al.,
344 2011; Knauth and Epstein, 1976; Marin et al., 2010; Marin-Carbonne et al., 2012). In addition, the diagenetic
345 transformations of opal-A to opal-CT and to microquartz can also lead to deviations from the equilibrium curve with
346 seawater (Ibarra et al., 2022). A recent study observed the consistency of triple O isotopes between modern altered
347 oceanic crust and Archean altered eclogite, thus precluding an Archean Ocean having a different O isotopic
348 composition from modern seawater (McGunnigle et al., 2022) and suggesting a stronger hydrothermal alteration in
349 the Archean. However, as shown by the present triple Si isotopes data, cherts can contain a significant fraction of
350 silica isotopically fractionated by kinetic processes, which was not considered in previous triple O isotopes studies.
351 This fraction of the chert would have a triple oxygen isotopic composition plotting far to the left of the equilibrium

352 curve with seawater in the $\Delta^{17}\text{O}-\delta^{18}\text{O}$ diagram (Fig. 6). It is not clear whether the kinetic signature of O isotopes in
353 silica can be erased by exchange with pore water or diagenetic fluid, while that of Si would be preserved. This might
354 be possible because of the low solubility of silica in water (water-rock interaction at 60°C would dissolve 215 ppm
355 SiO_2), the $\text{O}_{\text{fluid}}/\text{O}_{\text{rock}}$ ratio ($\approx 2.7 \times 10^4$) is 4 orders of magnitude higher than $\text{Si}_{\text{fluid}}/\text{Si}_{\text{rock}}$ (≈ 2.4). Nevertheless, it
356 suggests that bulk triple O isotopic measurements of cherts to reconstruct paleotemperatures should systematically
357 be associated to triple Si isotopic measurements to check for the presence of silica isotopically fractionated by kinetic
358 processes.

359 6. Conclusion

360 New high precision measurements of triple silicon isotopes in Precambrian cherts allow to identify small
361 deviations between pure equilibrium and pure kinetic mass-dependent isotopic fractionations. The chemical
362 contents, oxygen isotopes and the triple silicon isotopes in Jixian cherts imply that these cherts are made from
363 components having three sources: detrital quartz from the continents, hydrothermal quartz kinetically precipitated
364 from hydrothermal fluids close to the interface between seawater and the oceanic crust, and amorphous silica
365 precipitated at equilibrium from seawater. Archean cherts have Si isotopic compositions suggestive of successive
366 dissolution and reprecipitation of silica during diagenesis by both kinetic and equilibrium processes. This might cause
367 a bias when these samples are used for paleo-seawater temperature reconstructions from triple O isotopes,
368 depending on the extent to which the precursors of cherts had their O isotopic composition fractionated by kinetic
369 processes and on whether they were re-equilibrated with seawater during diagenesis. In any case, triple silicon
370 isotope data represent a useful additional criteria to select Precambrian cherts for paleotemperature
371 reconstructions. Finally, the present triple Si isotopic data are consistent with high temperatures for Archean oceans,
372 but a more precise statement would require further work to (i) calibration of the effect of temperature on β_{eq} for
373 $\alpha_{\text{silica-water}}$ and (ii) better determination of the triple Si isotopic fractionations for the other processes which
374 participate to the control of the Si isotopic composition of seawater, namely riverine inputs and authigenic clays
375 formation.

376 CRediT authorship contribution statement

377 **Haoxuan Sun:** methodology, analyses, interpretation, writing. **Marc Chaussidon:** design of the project,
378 interpretation, writing and funding. **François Robert:** interpretation, writing. **Shengyu Tian:** methodology. **Zhengbin**
379 **Deng:** methodology. **Frédéric Moynier:** interpretation, writing and funding.

380 Declaration of competing interest

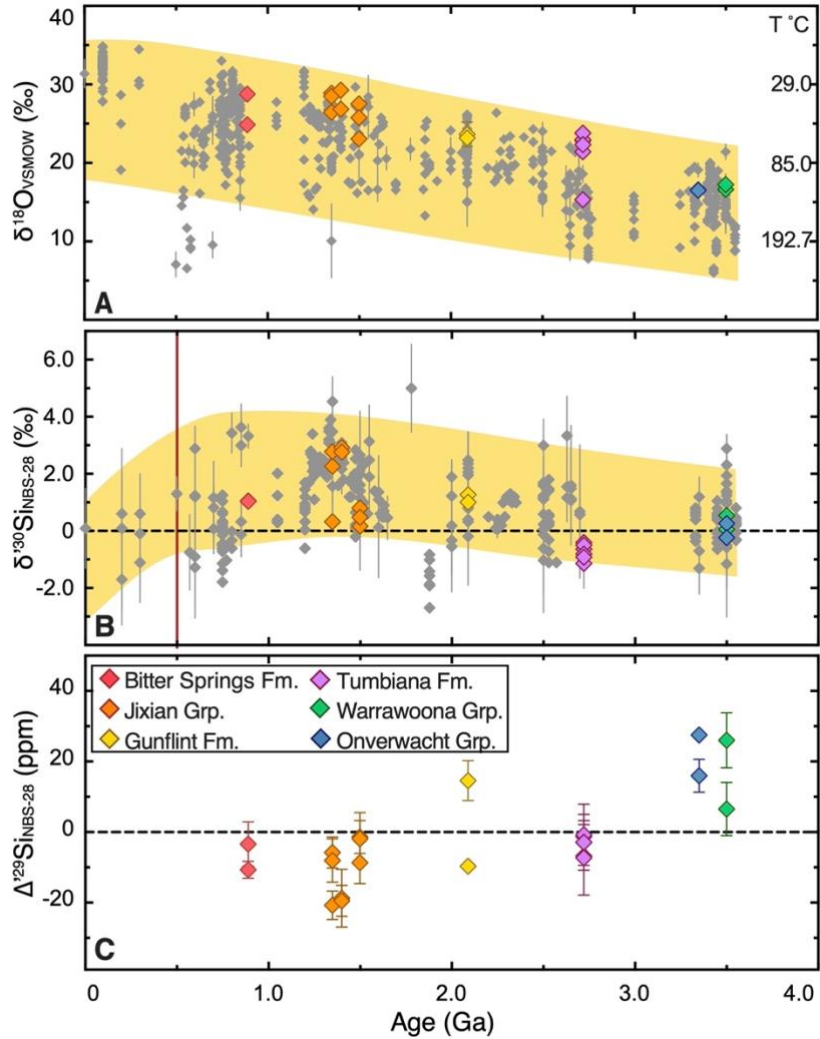
381 The authors declare that they have no known competing financial interests or personal relationships that
382 could have appeared to influence the work reported here.

383 **Acknowledgements**

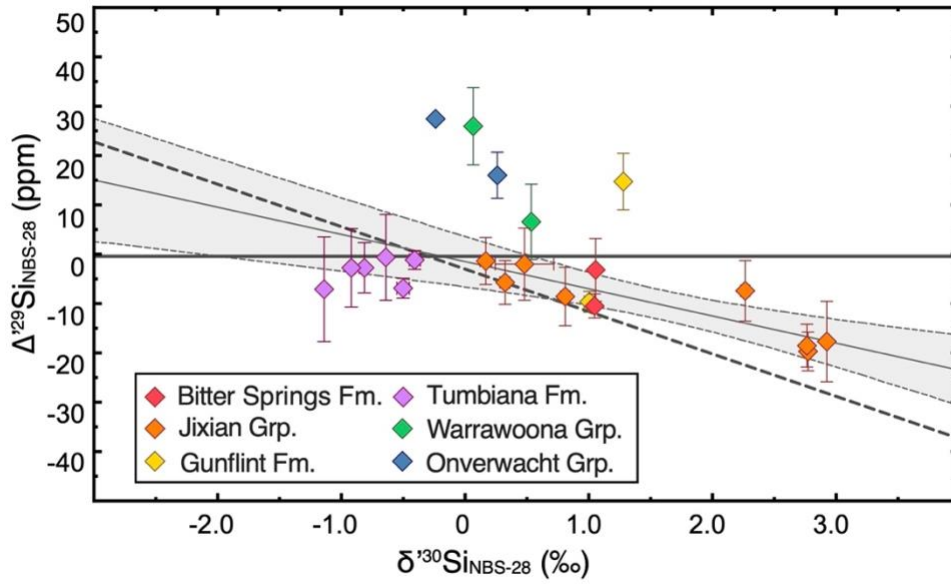
384 This work was supported by IGP multidisciplinary program PARI, by Paris–IdF region SESAME Grant no.
385 12015908, and by INSU-CNRS PNP grant 2022.

386 **Appendix. Supplementary material**

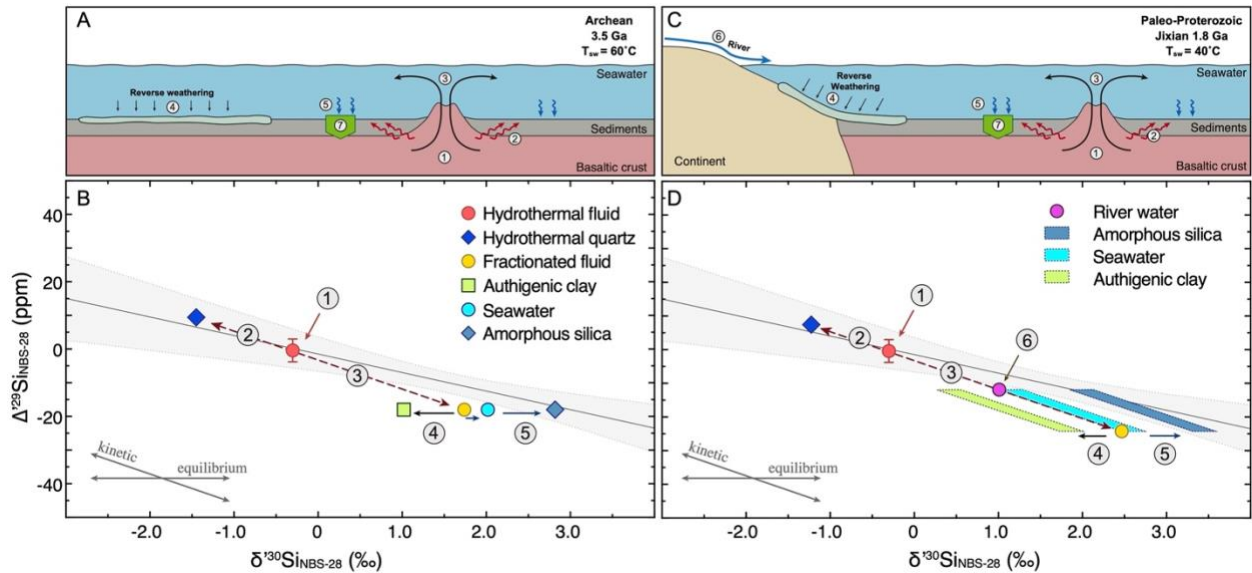
387 Supplementary material related to this article can be found below.



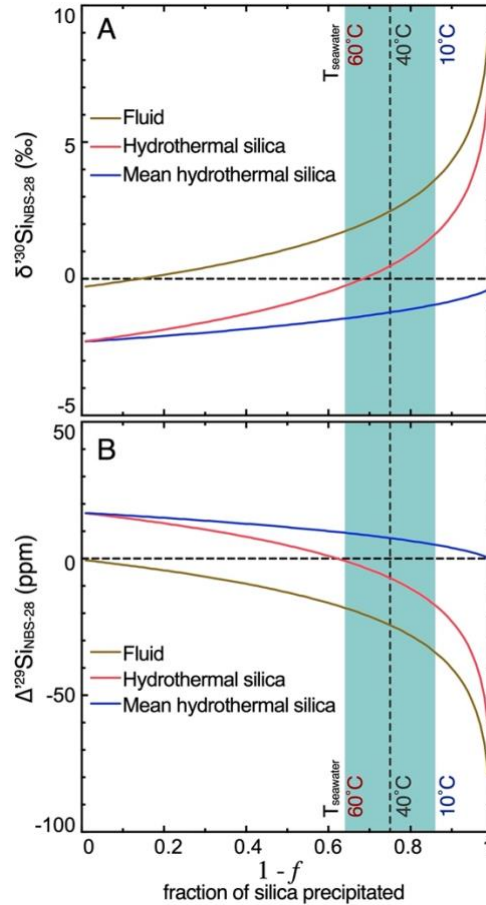
388 **Figure 1.** Oxygen and silicon isotopic compositions of Precambrian cherts versus age, $\delta^{18}\text{O}$ of microquartz in A, $\delta^{30}\text{Si}$
 389 in B and $\Delta^{129}\text{Si}$ in C. Data from this study (colored, Table 1) and from literature (in grey, Abraham et al., 2011;
 390 Chakrabarti et al., 2012; Ding et al., 2017; Hren et al., 2009; Knauth, 2005; Knauth and Epstein, 1976; Knauth and
 391 Lowe, 1978; Liljestrand et al., 2020; Marin et al., 2010; Marin-Carbonne et al., 2012; Robert and Chaussidon, 2006)
 392 are plotted with their two standard error ($2\sigma_{SE}$). Both $\delta^{18}\text{O}$ and $\delta^{30}\text{Si}$ values show large variations at a given age. The
 393 $\delta^{18}\text{O}$ and $\delta^{30}\text{Si}$ values of the cherts in this report are consistent with literature data. Precambrian cherts show
 394 significant variations of their $\Delta^{129}\text{Si}$, with a tendency for higher $\Delta^{129}\text{Si}$ for the oldest cherts. The yellow colored field
 395 are qualitative.



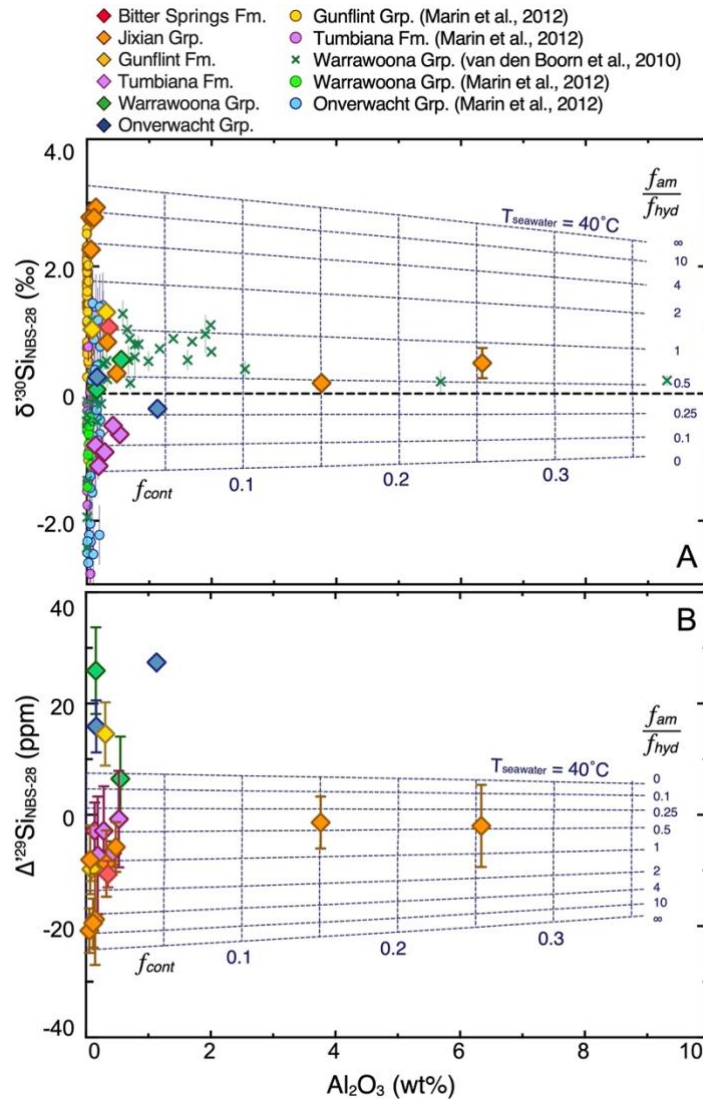
396 **Figure 2.** Details of triple silicon isotopic variations ($2\sigma_{SE}$) in cherts. The theoretical line (dashed black) for kinetic
 397 isotopic fractionation (slope -8.6) is considered to intersect the horizontal equilibrium isotopic fractionation line
 398 (solid black) at $\delta^{30}\text{Si} = -0.3\text{‰}$ (i.e. the value for bulk silicate Earth). The linear regression through Jixian cherts gives a
 399 slope of -5.51 ± 2.16 and a horizontal intercept of -0.262 ± 0.967 ($2\sigma_{SE}$), which correspond to a slope of $0.5123 \pm$
 400 0.0022 ($2\sigma_{SE}$) in $\delta^{129}\text{Si}$ - $\delta^{130}\text{Si}$ diagram (the grey zone representing the 95% confidence interval of the fit). The Jixian
 401 line is in between the theoretical equilibrium and kinetic isotopic fractionation lines.



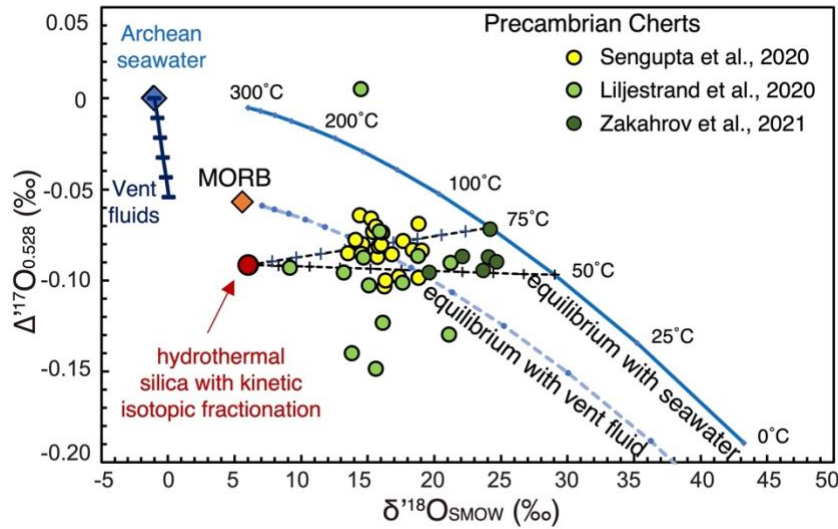
402 **Figure 3** Models for the origin of the triple silicon isotopic variations in early Archean cherts (A&B, seawater
 403 temperature at 60°C) and the Jixian cherts (C&D, seawater temperature at 40°C). ① Hydrothermal leaching of Si
 404 from the oceanic basaltic crust ($\delta^{30}\text{Si} = -0.30 \pm 0.02$ ‰) takes place with no Si isotopic fractionation. The kinetic Si
 405 isotopic fractionation during the precipitation of hydrothermal quartz (assuming $\Delta^{30}\text{Si}_{\text{quartz-fluid}} = -2.0$ ‰ and following
 406 a trajectory with a slope of -8.6) will ② deplete ^{30}Si in hydrothermal quartz relative to hydrothermal fluids and by
 407 mass balance will ③ release into seawater a strongly kinetically fractionated fluid enriched in ^{30}Si . ④ Reverse
 408 weathering and ⑤ precipitation of amorphous silica take place to maintain dissolved Si saturated in seawater. Si
 409 isotopic fractionations for both processes are expected to be at equilibrium ($\Delta^{30}\text{Si}_{\text{chert-sw}} = +0.8$ ‰ see *Appendix*, and
 410 $\Delta^{30}\text{Si}_{\text{clay-chert}} = -2$ ‰, Trower and Fisher, 2018). Considering that the uptake of dissolved Si by reverse weathering can
 411 represent up to 60% of the total Si uptake, $\delta^{30}\text{Si}_{\text{sw}}$ will increase by ≈ 0.4 ‰. Since the late Archean, the growth of
 412 continents made that ⑥ rivers became another important Si flux to seawater. The blue field in D represents the
 413 possible Si isotopic composition of seawater in Jixian times (assuming kinetic Si isotopic fractionation during
 414 continental weathering and average $\delta^{30}\text{Si}_{\text{river}} = 1$ ‰, see refs in text). ⑦ Formation of chert.



415 **Figure 4.** Fractionation of Si isotopes during precipitation of hydrothermal quartz due to cooling of hydrothermal
 416 fluids ascending in the oceanic crust (panel A for $\delta^{30}\text{Si}$, panel B for $\Delta^{129}\text{Si}$). The Si isotopic composition of the fluid is
 417 given by the Rayleigh equation $\delta^{30}\text{Si}_{\text{fluid}} = \delta^{30}\text{Si}_{\text{initial}} + \Delta^{30}\text{Si}_{\text{solid-fluid}} \times \ln(f)$, with f the fraction of Si remaining in the fluid
 418 at the temperature of seawater (f being the ratio of the solubility of amorphous silica at the temperature of seawater
 419 to the solubility of hydrothermal quartz at the temperature of the initial fluid, Robert and Chaussidon (Robert and
 420 Chaussidon, 2006). The initial hydrothermal fluid is assumed to have a temperature of 300°C and the Si isotopic
 421 composition of fresh oceanic crust (i.e., the same than BHVO-2, $\delta^{30}\text{Si} = -0.3\text{‰}$ and $\Delta^{129}\text{Si} = 0$). The value of f ranges
 422 from 0.14 to 0.36 (blue field in Fig S8) for a seawater temperature ranging from 10 to 60°C . Taking a value of $\Delta^{30}\text{Si}_{\text{solid-}}$
 423 fluid of -2.00‰ (Chen et al., 2020) and a θ value characteristic of a kinetic process (0.5092), this gives a range for $\delta^{30}\text{Si}$
 424 and $\Delta^{129}\text{Si}$ values of hydrothermal silica from -0.94‰ to -1.45‰ and from 0.05 to 0.10, respectively. Consequently,
 425 dissolved Si delivered to the oceans will have $\delta^{30}\text{Si}$ and $\Delta^{129}\text{Si}$ values from 3.63‰ to 1.74‰ and from -34 to -18 ,
 426 respectively.



427 **Figure 5.** Constraints from Si isotopic compositions and Al_2O_3 contents on the fraction of the three possible sources
 428 of silica in the precursors of Precambrian cherts [present data and data from (Marin-Carbonne et al., 2012; Van den
 429 Boorn et al., 2010)]: detrital continental silica (f_{cont} shown as vertical dashed lines calculated for a continental end
 430 member with 60% silica and 25% Al_2O_3), amorphous silica considered to have precipitated from seawater at 40°C
 431 (f_{am}), and hydrothermal silica (f_{hyd}). The horizontal dashed lines show the ratio $f_{\text{am}}/f_{\text{hyd}}$. Note the large variations
 432 among Precambrian cherts in the $f_{\text{am}}/f_{\text{hyd}}$ ratios. Note also that most of the present Archean cherts have $\Delta^{129}\text{Si}$ that
 433 cannot be explained by this mixing model and require additional Si isotopic fractionations.



434 **Figure 6.** Possible effects of the presence of oxygen kinetic isotopic fractionations on the triple oxygen isotopes
 435 systematics of Archean cherts. The linearized delta notation is used with $\delta^{xx}O=1000 \times \ln(\delta^{xx}O/1000+1)$, where ^{xx}O
 436 represents ^{17}O and ^{18}O , and $\Delta^{17}O = \delta^{17}O - 0.528 \times \delta^{18}O$. To keep the diagram simple, we have chosen 3 representative
 437 sets of data for Precambrian cherts from (Liljestrand et al., 2020; Sengupta et al., 2020; Zakharov et al., 2021). Mid
 438 Ocean Ridge Basalt (MORB) representing unaltered oceanic crust is from (Pack and Herwartz, 2014; Sharp et al.,
 439 2016). Vent fluids corresponding to a mixture between seawater and hydrothermal fluids at equilibrium with MORB
 440 are shown following the approach of (Zakharov et al., 2021). The red dot is for a possible oxygen isotopic composition
 441 of hydrothermal silica fractionated by a kinetic isotopic fractionation (using 0.515 instead of 0.528 for the
 442 relationship between $\delta^{17}O$ and $\delta^{18}O$). The presence in various proportions of such hydrothermal silica in a chert
 443 with microquartz formed at equilibrium with seawater between 50 and 75°C (mixing relationships shown as dashed
 444 black lines) could explain part of the range observed for the triple oxygen isotopic compositions of Precambrian
 445 cherts.

Sample	Age (Ga)	MC-ICP-MS										SIMS bulk							
		$\delta^{129}\text{Si}$	2sd	2se	$\delta^{130}\text{Si}$	2sd	2se	$\Delta^{129}\text{Si}$	2sd	2se	n	$\delta^{18}\text{O}$	2se	n	$\delta^{130}\text{Si}$	se			
Bitter Springs Fm.																			
BitterSprings 5 of 5/11/90	0.89	^a	0.544	0.012	0.004	1.057	0.023	0.008	-3	18	6	8	24.9	0.8	^a	10	3.33	0.21	^a
BitterSprings 5 of 5/11/90_rp			0.532	0.040	0.016	1.047	0.069	0.028	-10	6	2	6	28.8	0.3					
<i>BitterSprings 5 of 5/11/90 Average</i>	0.89	^a	0.538	<i>0.018</i>	<i>0.012</i>	1.052	<i>0.014</i>	<i>0.010</i>	-7	<i>10</i>	<i>7</i>	<i>2</i>							
Jixian																			
Jixian 2A of 8/18/83	1.35	^a	0.162	0.059	0.021	0.324	0.111	0.039	-6	13	5	8	26.45	0.33		10			
Jixian 2b of 8-16-83	1.35	^a	1.166	0.051	0.025	2.267	0.076	0.038	-7	12	6	4	28.92	0.12		10	3.48	0.55	^a
Jixian 3b of 8-16-83	1.35	^a	1.416	0.038	0.011	2.772	0.072	0.021	-20	14	4	12	28.49	0.37		10	2.45	0.79	^a
Jixian 5a of 8/12/93	1.40	^a	1.497	0.028	0.014	2.925	0.029	0.014	-18	16	8	4	26.84	0.17		10			
Jixian 5b of 8/12/93	1.40	^a	1.414	0.052	0.015	2.766	0.092	0.027	-18	15	4	12	29.32	0.20		10			
Jixian 2 of 8/18/83	1.50	^a	0.412	0.094	0.021	0.812	0.169	0.038	-9	27	6	20	27.52	0.17		10	2.14	0.31	^a
Jixian 8/18/83	1.50	^a	0.087	0.082	0.024	0.170	0.158	0.045	-1	16	5	12	25.82	0.98		9			
Jixian 8 of 8/18/83	1.50	^a	0.248	0.329	0.116	0.483	0.665	0.235	-2	21	7	8	23.09	0.64		6	1.16	0.29	^a
Gunflint Fm.																			
Gunflint PPRG134	2.09	^a	0.678	0.011	0.005	1.280	0.026	0.013	15	11	6	4	23.6	1.6	^a		0.83	0.55	^a
Gunflint 3 of 6/30/84			0.500	0.018	0.009	0.986	0.039	0.020	-11	15	7	4							
			0.524	0.043	0.025	1.029	0.085	0.049	-9	7	4	3							
<i>Gunflint 3 of 6/30/84 Average</i>	2.09	^a	0.512	<i>0.035</i>	<i>0.024</i>	1.008	<i>0.061</i>	<i>0.043</i>	-10	<i>3</i>	<i>2</i>	<i>2</i>	23.3	1.0	^b		0.8	0.6	^b
Tumbiana																			
Tumbiana 1 of 07/06/90			-0.222	0.029	0.008	-0.427	0.045	0.013	0	14	4	12							
			-0.200	0.018	0.011	-0.383	0.022	0.012	-2	13	7	3							
<i>Tumbiana 1 of 07/06/90 Average</i>	2.72	^b	-0.211	<i>0.030</i>	<i>0.021</i>	-0.405	<i>0.063</i>	<i>0.044</i>	-1	<i>3</i>	<i>2</i>	<i>2</i>	18.6	1.1	^b		-1.10	0.90	^a
Tumbiana 1 of 07/06/90_P1			-0.331	0.033	0.013	-0.637	0.029	0.012	-1	21	9	6	15.33	0.62		10			
Tumbiana 1 of 07/06/90_P2			-0.266	0.068	0.028	-0.501	0.123	0.050	-7	5	2	6	22.88	0.45		7			
Tumbiana 1 of 07/06/90_P3			-0.422	0.037	0.012	-0.810	0.067	0.022	-3	15	5	9	22.97	0.34		7			
Tumbiana 1 of 07/06/90_P4			-0.597	0.029	0.012	-1.139	0.060	0.025	-7	26	11	6	23.81	0.68		8			
Tumbiana 1 of 07/06/90_P5			-0.477	0.038	0.015	-0.916	0.067	0.027	-3	20	8	6	22.34	0.56		10			
Onverwacht Grp.																			
Onverwacht PPRG198	3.35	^b	0.151	0.054	0.019	0.261	0.084	0.030	16	13	5	8	16.7	0.7	^b		-0.20	0.70	^b
Onverwacht 2 of 16/09/65	3.35	^b	-0.093	0.098	0.020	-0.234	0.188	0.038	28	19	4	24							
			-0.098	0.016	0.009	-0.241	0.016	0.010	27	10	6	3							
<i>Onverwacht 2 of 16/09/65 Average</i>			-0.095	0.006	0.004	-0.237	0.010	0.007	27	<i>1</i>	<i>1</i>	<i>2</i>	14.8	0.5	^b		-1.30	0.90	^b
Warrawoona Grp.																			
Warrawoona PPRG006	3.50	^a	0.284	0.021	0.010	0.536	0.043	0.022	7	15	8	4	14.3	0.5	^b		-0.20	0.70	^b
Warrawoona PPRG013	3.50	^a	0.061	0.023	0.012	0.069	0.020	0.010	26	16	8	4	13.6	1.7	^a		1.40	0.32	^a
Terrestrial standard																			
BHVO-2			-0.156	0.058	0.009	-0.301	0.107	0.016	0	23	3	43							
BCR-2			-0.109	0.075	0.037	-0.206	0.144	0.072	-2	11	5	4							
BIR-1a			-0.124	0.126	0.063	-0.233	0.217	0.108	-4	15	8	4							
GSP-2			-0.121	0.140	0.070	-0.238	0.232	0.116	2	22	11	4							
AGV-2			-0.101	0.071	0.035	-0.178	0.143	0.071	-9	14	7	4							

446 **Table 1.** Bulk silicon and oxygen isotopic composition of cherts and terrestrial rock standards. Data from ^aRobert and Chaussidon, 2006 and ^bMarin-Carbonne et al., 2012

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