The $\delta^{30}\text{Si}$ peak value discovered in middle Proterozoic chert and its implication for environmental variations in the ancient ocean

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The silicon isotope composition of chert has recently been used to study the historic evolution of the global ocean. It has been suggested that Precambrian cherts have much higher $\delta^{30}\text{Si}$ values than Phanerozoic cherts do and that the former show an increasing trend from 3.5 to 0.85 Ga, reflecting a decrease in ocean temperatures. However, cherts have various origins, and their isotopic compositions might be reset by metamorphic fluid circulation; thus, different types of cherts should be distinguished. Here, we present a new set of $\delta^{30}\text{Si}$ data for cherts from early and middle Proterozoic carbonate rocks from Northern China. We found that cherts of 1.355–1.325 Ga show a peak range of 2.2–3.9‰. Based on these results, we propose that from the Archean to the middle Proterozoic, there was a drastic decrease in silicon content and an increase in the $\delta^{30}\text{Si}$ value in ocean water due to a temperature decrease and biological activity increase. After that period, the silicon content of the ocean was limited to a low level by a high degree of biological absorption, and their $\delta^{30}\text{Si}$ values varied in a small range around a significantly lower value.

Chert is a sedimentary rock composed mainly of microcrystalline quartz. It occurs in sedimentary strata from the early Archean to the present. Its chemical and isotopic characteristics have been widely investigated to study the conditions of its formation. Recently, Si isotopes in chert have been used as an important tracer of environmental conditions in the global ocean$^{1–18}$. Song and Ding (1990) suggested distinguishing sedimentary facies of chert with silicon isotope compositions$^{1}$. Ding et al. (1996) indicated that different genetic types of cherts have different silicon isotope characters$^{2}$. They discussed variations in silicon content and silicon isotope composition in marine water according to the data from chert formed in shallow marine environments. According to the silicon isotope variation of chert, Robert and Chaussidon (2006) developed a temperature-evolution curve for the Precambrian ocean$^{3}$. It has been suggested that Precambrian cherts have much higher $\delta^{30}\text{Si}$ values than Phanerozoic cherts and that the former show a generally increasing trend from 3.5 to 0.85 Ga, thus reflecting a decrease in seawater temperature$^{3}$. However, these statements have been challenged because cherts can have various origins and their isotopic compositions might have been reset by metamorphic fluid circulation$^{4–9}$. Thus, different types of cherts need to be considered separately$^{4–9,12}$ because their isotope composition might record various distinct processes$^{13–18}$. In addition, the factors that affect silicon isotope composition of chert have been investigated in detail$^{13–18}$. It was found that peritidal cherts are enriched in $^{30}\text{Si}$, but that basinal cherts, which are associated with banded iron formations (BIF), are depleted in $^{30}\text{Si}$; this difference is attributed to Si having been derived from hydrothermal sources in the BIFs$^{10}$. Now, it is widely accepted that the formation of chert is a complicated process and that the Si isotope composition of chert is dependent on the relative contributions of various Si sources and the effects of different forming processes$^{5–18}$. However, the relative contributions of the various Si sources to the global ocean vary throughout geological history. Thus, specific types of chert might be representative for reconstructing the Si isotope composition of the ocean for different geological periods. For example, during the Archean period, sea-floor weathering and submarine hydrothermal fluids dominated the Si input to the ocean, and continent inputs were negligible; thus, the Si isotope compositions of quartz bands in BIF are likely the best approach for tracing the Si isotope compositions of the ocean. In contrast, in the Proterozoic and Phanerozoic periods, the Si...
input from the continent to the ocean became dominant, and the Si input from sea-floor weathering and sub-
marine hydrothermal fluids became less prevalent; thus, peritidal chert may be more significant in tracing the Si
isotope composition of the ocean. To date, many studies have investigated the silicon isotope composition of silica
in BIF to examine the environmental conditions of the Archean ocean2–9,11–14. However, studies specifically tar-
geting the silicon isotope composition of cherts formed in shallow marine environment are relatively rare10. More
systematic and detailed Si isotope studies on this aspect must be undertaken to reconstruct the silicon content
and silicon isotope composition in the ancient ocean and understand the historic evolution of the global ocean.

We collected a suite of samples of carbonate rocks containing chert bands and nodules from the early
Proterozoic Huuto Group19 (2.35–2.20 Ga) and the middle Proterozoic Changcheng and Jixian Systems20,21 (1.63–
1.20 Ga) in Northern China (Fig. 1). These cherts were selected because they showed good preservation of their
original structure and composition (Figs 2 and 3); i.e., no obvious effects of metamorphism or weathering were
found in the selected samples. The Si and O isotopic compositions of the chert and the C and O isotopic compo-
sitions of dolomite were studied systematically.

Figure 1. Schematic geological maps of sampling area. (a) Map of the Jixian area, Hebei province20; (b) Map
of the Shisanlin area, Beijing21; (c) Map of the Wutai area, Shanxi province19; (d) A sketch map showing the
locations of sampling areas. The sampling areas of Jixian, Shisanlin and Wutai are indicated by red solid cycles
in the map. 1-Quaternary strata; 2-Phanerozoic strata; 3-Upper Proterozoic Qingbaikou System; 4-Tieling Fm.,
Jixian system; 5-Hongshuizhuang Fm., Jixian System; 6-Wumishan Fm., Jixian System; 7-Yangzhuan Fm.,
Jixian System; 8-Gaoyuzhuang Fm., Changcheng System; 9-Dahongyu Fm., Changcheng System;
10-Tuanshanzhi Fm., Changcheng System; 11-Chuanlinggou Fm., Changcheng System; 12-Changzou Fm.,
Changcheng System; 13-Middle Proterozoic strata; 14-Sijizhuang Fm., Huuto Group; 15-Doucun Fm.,
Huuto Group; 16-Dongye Fm., Huuto Group; 17-Guojiagai Fm., Huuto Group; 18- later Archean Wutai strata;
19-Granite; 20-Fault; 21- Sampling profiles in Jixian (a, A-A), Shisanlin (b, B-B) and Wutai (c, C-C). The
software CorelDRAW X3 (13.0.0.667) was used to create the maps. The URL is http://www.corel.com.
Results
The Si and O isotope compositions of the cherts and the C and O isotope compositions of dolomites obtained in this study are listed in Table 1 and shown in Fig. 4. All isotope compositions are reported in delta-notation relative to a standard material, i.e.,

$$\delta A(\text{‰}) = \left( \frac{R_{\text{Sa}}}{R_{\text{St}}} - 1 \right) \times 10^3 \quad \text{(1)}$$

where A represents the isotope, R represents the isotope ratio, the subscript Sa refers to the sample and St refers to the standard. For the Si isotope compositions, A means $^{30}\text{Si}$, R means $^{30}\text{Si}/^{28}\text{Si}$, St means NBS-28. For the O isotope composition, A means $^{18}\text{O}$, R means $^{18}\text{O}/^{16}\text{O}$, and St can be either V-SMOW (for chert and dolomite) or V-PDB (for dolomite). For the C isotope composition, A means $^{13}\text{C}$, R means $^{13}\text{C}/^{12}\text{C}$, and St means V-PDB.

The $\delta^{13}\text{C}_{\text{V-PDB}}$ and $\delta^{18}\text{O}_{\text{V-PDB}}$ values of dolomites. The obtained $\delta^{13}\text{C}_{\text{V-PDB}}$ values of dolomites range from $-2.5\%_\circ$ to $1.9\%_\circ$, with an average of $-0.36 \pm 0.82$ (1 SD) $\%_\circ$. The obtained $\delta^{18}\text{O}_{\text{V-PDB}}$ values of dolomites range from $-12.9\%_\circ$ to $-3.5\%_\circ$, with an average of $-7.11 \pm 2.15$ (1 SD) $\%_\circ$. These values are similar to those reported in previous studies\textsuperscript{22,23}, reflecting their normal sedimentary origin in a shallow marine environment. The $\delta^{18}\text{O}_{\text{V-PDB}}$ values indicate that the dolomite had been influenced to some degree by diagenesis.

The $\delta^{18}\text{O}_{\text{V-SMOW}}$ values of cherts. The $\delta^{18}\text{O}_{\text{V-SMOW}}$ values of the chert samples range from $14.3\%_\circ$ to $27.8\%_\circ$, with an average of $23.0 \pm 3.5$ (1 SD) $\%_\circ$. These results also show that they were formed in a shallow marine environment but might have been slightly affected by diagenesis.
The δ30Si values of the cherts collected in this study range from 0.1‰ to 3.9‰. Among them, the early Proterozoic cherts show lower δ30Si values, ranging from 0.1‰ to 1.3‰, with an average of 0.75 ± 0.43‰ (1 SD), compared to middle Proterozoic cherts ranging from 0.5‰ to 3.9‰, with an average of 2.22 ± 0.74‰ (1 SD). Furthermore, a peak range in δ30Si [2.2–3.9‰, averaging 3.12 ± 0.56‰ (1 SD)] is observed in the cherts of 1.325–1.355 Ga (Fig. 4). In addition, the δ30Si variation of chert can also be observed on a millimetre scale. For example, 4 chert bands in sample JX-26 and 5 chert bands in sample JX-27 show δ30Si variations of 2.3∼3.9‰ and 3.1∼3.6‰, respectively (Table 1).

Discussion
The increasing trend of δ30Si from the early Proterozoic to middle Proterozoic is consistent with the trends reported by previous studies4,5,8–10. However, together with the new data provided in this study, the middle Proterozoic δ30Si peak becomes a prominent feature in the Si isotope record of Precambrian cherts, which implies major environmental variations in the ancient ocean (Fig. 4).

Combining data obtained using SiF4 and MC-ICP-MS methods in this study and previous studies10,24–30, the δ30Si variation trend from the late Archean to present is plotted for chert that formed in shallow marine environments (Fig. 5). The upper limit of δ30Si values of chert increases gradually from 1.8‰ at 2.53 Ga to 3.9‰ at 1.335 Ga and then decreases drastically to 2.0‰ at 1.104 Ga. After 1.104 Ga, the upper limit of δ30Si values for chert fluctuates between 1.5‰ and 2.5‰.

Chert is normally formed by the recrystallization of a precipitated amorphous silica precursor in the diagenetic process. To test the possibility of using O and Si isotope compositions of chert to trace those of contemporary
| Sample No. | Sample type | Strata                  | Age (Ma) | CaMg (CO₃)₂ | δ¹³C_V-PDB (‰) | δ¹⁸O_V-PDB (‰) | δ¹⁸O_V-SMOW (‰) | δ¹⁸O_V-SMOW (‰) | δ³⁰Si_NBS-28 (‰) | δ³⁰Si_NBS-28 (‰) | δ³⁰Si_NBS-28 (‰) |
|------------|-------------|-------------------------|----------|--------------|----------------|----------------|-----------------|-----------------|----------------|----------------|----------------|
| HT-03      | Purple-red fine banded cherty Dol. | Hebiancun Fm., Hutuo Gr. | 2350     | 0.6          | −8.3           | 22.4           | 19.8            | 1.0             |                |                |                |
| HT-04      | Purple-red cherty Dol. | Hebiancun Fm., Hutuo Gr. | 2340     | 0.9          | −8.1           | 22.6           | 19.6            | 1.2             |                |                |                |
| HT-05      | Purple-red fine banded cherty Dol. | Hebiancun Fm., Hutuo Gr. | 2330     | 0.9          | −8.1           | 22.6           | 19.6            | 1.0             |                |                |                |
| HT-06      | Yellow fine banded cherty Dol. | Hebiancun Fm., Hutuo Gr. | 2320     | 1.6          | −9.4           | 21.2           | 17.8            | 1.3             |                |                |                |
| HT-07      | Purple-red fine banded cherty Dol. | Hebiancun Fm., Hutuo Gr. | 2310     | 1.9          | −9.4           | 21.2           | 18.7            | 1.1             |                |                |                |
| HT-08      | Grey banded cherty Dol. | Hebiancun Fm., Hutuo Gr. | 2300     | 1.2          | −9.3           | 21.3           | 19.4            | 1.2             |                |                |                |
| HT-09      | Dark grey fine banded cherty Dol. | Hebiancun Fm., Hutuo Gr. | 2290     | −0.9         | −8.6           | 22.0           | 23.0            | 0.5             |                |                |                |
| HT-10      | Purple-red cherty Dol. | Hebiancun Fm., Hutuo Gr. | 2280     | −0.3         | −6.8           | 23.9           | 19.9            | 1.0             |                |                |                |
| HT-11      | Dark grey cherty Dol. | Hebiancun Fm., Hutuo Gr. | 2270     | −1.7         | −9.2           | 21.4           | 21.5            | 0.2             |                |                |                |
| HT-12      | Grey fine banded cherty Dol. | Hebiancun Fm., Hutuo Gr. | 2260     | 0.6          | −9.4           | 21.2           | 18.2            | 0.3             |                |                |                |
| HT-14      | Grey banded cherty Dol. | Jianan Fm., Hutuo Gr. | 2250     | 0.4          | −8.3           | 22.3           | 19.3            | 0.4             |                |                |                |
| HT-15      | Dark grey cherty Dol. | Jianan Fm., Hutuo Gr. | 2240     | −2.5         | −12.9          | 17.6           | 17.6            | 0.1             |                |                |                |
| HT-18      | Bright purple cherty Dol. | Daguanshan Fm., Hutuo Gr. | 2200     | 0.5          | −9.5           | 21.0           | 19.4            | 0.5             |                |                |                |

Changcheng and Jixian Systems in the Jixian profile

| Sample No. | Sample type | Strata                  | Age (Ma) | CaMg (CO₃)₂ | δ¹³C_V-PDB (‰) | δ¹⁸O_V-PDB (‰) | δ¹⁸O_V-SMOW (‰) | δ¹⁸O_V-SMOW (‰) | δ³⁰Si_NBS-28 (‰) | δ³⁰Si_NBS-28 (‰) | δ³⁰Si_NBS-28 (‰) |
|------------|-------------|-------------------------|----------|--------------|----------------|----------------|-----------------|-----------------|----------------|----------------|----------------|
| JX-40-7    | Black siliceous bands | Wumishan Fm. (top), Jixian System | 1230    | 0.9          | −7.2           | 23.4           | 25.3            | 2.7             |                |                |                |
| JX-40-6    | Black siliceous bands | Wumishan Fm. (top), Jixian System | 1230    | 0.7          | −9.4           | 21.2           | 27.2            | 2.8             |                |                |                |
| JX-37-4    | Black siliceous bands | Wumishan Fm. (top), Jixian System | 1240    | 1.0          | −11.1          | 19.4           | 26.0            | 2.1             |                |                |                |
| JX-37-3    | Black siliceous bands | Wumishan Fm. (top), Jixian System | 1240    | 0.7          | −9.3           | 21.2           | 25.9            | 2.7             |                |                |                |
| JX-37-2    | Black siliceous bands | Wumishan Fm. (top), Jixian System | 1240    | 1.0          | −9.0           | 21.6           | 26.0            | 2.6             |                |                |                |
| JX-37-1    | Black siliceous bands | Wumishan Fm. (top), Jixian System | 1240    | 0.7          | −9.2           | 21.3           | 26.7            | 2.4             |                |                |                |
| JX-36-12   | Siliceous bands in dolomite | Wumishan Fm., Jixian System | 2nd member | −0.3        | −10.8          | 19.7           | 25.3            | 2.3             |                |                |                |
| JX-36-11   | Siliceous bands in dolomite | Wumishan Fm., Jixian System | 2nd member | −0.4        | −8.4           | 22.2           | 25.3            | 2.4             |                |                |                |
| JX-36-10   | Siliceous bands in dolomite | Wumishan Fm., Jixian System | 2nd member | −0.7        | −9.3           | 21.3           | 25.8            | 2.4             |                |                |                |
| JX-36-9    | Siliceous bands in dolomite | Wumishan Fm., Jixian System | 2nd member | −0.5        | −7.7           | 22.9           | 26.6            | 2.2             |                |                |                |
| JX-36-7    | Siliceous bands in dolomite | Wumishan Fm., Jixian System | 2nd member | −0.5        | −6.2           | 24.5           | 26.0            | 2.3             |                |                |                |
| JX-36-6    | Siliceous bands in dolomite | Wumishan Fm., Jixian System | 2nd member | −0.7        | −6.4           | 24.2           | 26.4            | 2.4             |                |                |                |
| JX-36-5    | Siliceous bands in dolomite | Wumishan Fm., Jixian System | 2nd member | −0.7        | −6.3           | 24.4           | 26.0            | 2.4             |                |                |                |
| JX-36-3    | Siliceous bands in dolomite | Wumishan Fm., Jixian System | 2nd member | −0.7        | −7.3           | 23.4           | 25.8            | 2.4             |                |                |                |

Continued
| Sample No. | Sample type                      | Strata                          | Age (Ma) | $\delta^{13}$CV-PDB (%) | $\delta^{18}$OV-PDB (%) | $\delta^{18}$OV-SMOW (%) | $\delta^{18}$OV-SMOW (%) | $\delta^{30}$SiNBS-28 (%) |
|------------|----------------------------------|---------------------------------|----------|--------------------------|--------------------------|-----------------------------|-----------------------------|----------------------------|
| JX-36-1    | Siliceous bands in dolomite      | 2nd member, Wumishan Fm., Jixian System | 1250     | −0.8                     | −10.6                    | 20.0                        | 25.4                        | 2.2                        |
| JX-34      | Siliceous bands in dolomite      | 2nd member, Wumishan Fm., Jixian System | 1270     | −1.1                     | −5.9                     | 24.8                        | 25.1                        | 2.2                        |
| JX-33-12   | Siliceous bands in dolomite      | 2nd member, Wumishan Fm., Jixian System | 1280     | −1.2                     | −11.1                    | 19.5                        | 25.8                        | 2.2                        |
| JX-33-11   | Siliceous bands in dolomite      | 2nd member, Wumishan Fm., Jixian System | 1280     | −1.0                     | −9.6                     | 20.9                        | 26.3                        | 2.5                        |
| JX-33-10   | Siliceous bands in dolomite      | 2nd member, Wumishan Fm., Jixian System | 1280     | −1.0                     | −11.0                    | 19.6                        | 25.3                        | 2.4                        |
| JX-33-8    | Siliceous bands in dolomite      | 2nd member, Wumishan Fm., Jixian System | 1280     | −1.2                     | −9.4                     | 21.2                        | 25.1                        | 2.3                        |
| JX-33-7    | Siliceous bands in dolomite      | 2nd member, Wumishan Fm., Jixian System | 1280     | −1.2                     | −11.8                    | 18.7                        | 24.7                        | 2.4                        |
| JX-33-6    | Siliceous bands in dolomite      | 2nd member, Wumishan Fm., Jixian System | 1280     | −1.1                     | −8.9                     | 21.6                        | 24.6                        | 2.3                        |
| JX-33-5    | Siliceous bands in dolomite      | 2nd member, Wumishan Fm., Jixian System | 1280     | −1.1                     | −8.8                     | 21.8                        | 25.2                        | 2.2                        |
| JX-33-3    | Siliceous bands in dolomite      | 2nd member, Wumishan Fm., Jixian System | 1280     | −1.0                     | −8.1                     | 22.5                        | 26.1                        | 2.3                        |
| JX-32      | Siliceous bands in dolomite      | 2nd member, Wumishan Fm., Jixian System | 1290     | −1.2                     | −6.7                     | 23.9                        | 24.6                        | 2.1                        |
| JX-27-6    | Siliceous bands in dolomite      | 2nd member, Wumishan Fm., Jixian System | 1325     | −0.6                     | −6.5                     | 24.1                        | 26.8                        | 3.2                        |
| JX-27-5    | Siliceous bands in dolomite      | 2nd member, Wumishan Fm., Jixian System | 1325     | −0.8                     | −7.6                     | 23.1                        | 27.3                        | 3.5                        |
| JX-27-4    | Siliceous bands in dolomite      | 2nd member, Wumishan Fm., Jixian System | 1325     | −0.7                     | −6.6                     | 24.1                        | 27.8                        | 3.1                        |
| JX-27-3    | Siliceous bands in dolomite      | 2nd member, Wumishan Fm., Jixian System | 1325     | −0.6                     | −6.1                     | 24.6                        | 27.7                        | 3.2                        |
| JX-27-2    | Siliceous bands in dolomite      | 2nd member, Wumishan Fm., Jixian System | 1325     | −0.1                     | −7.5                     | 23.2                        | 27.6                        | 3.6                        |
| JX-26-6    | Siliceous bands in dolomite      | 2nd member, Wumishan Fm., Jixian System | 1335     | −0.9                     | −5.9                     | 24.8                        | 25.3                        | 3.9                        |
| JX-26-4    | Siliceous bands in dolomite      | 2nd member, Wumishan Fm., Jixian System | 1335     | −0.3                     | −5.9                     | 24.7                        | 25.2                        | 3.9                        |
| JX-26-3    | Siliceous bands in dolomite      | 2nd member, Wumishan Fm., Jixian System | 1335     | −0.2                     | −6.0                     | 24.7                        | 24.2                        | 3.1                        |
| JX-26-2    | Siliceous bands in dolomite      | 2nd member, Wumishan Fm., Jixian System | 1335     | −0.2                     | −6.2                     | 24.5                        | 23.1                        | 2.3                        |
| JX-25      | Siliceous bands in dolomite      | 2nd member, Wumishan Fm., Jixian System | 1345     | −0.7                     | −7.1                     | 23.5                        | 25.2                        | 2.7                        |
| JX-20-8    | Siliceous bands in dolomite (with bitumen) | Yangzhuang Fm., Jixian System | 1400     | −1.0                     | −7.6                     | 23.0                        | 21.7                        | 2.6                        |
| JX-20-7    | Siliceous bands in dolomite (with bitumen) | Yangzhuang Fm., Jixian System | 1400     | −1.3                     | −7.6                     | 23.0                        | 23.3                        | 3.1                        |
| JX-20-6    | Siliceous bands in dolomite (with bitumen) | Yangzhuang Fm., Jixian System | 1400     | −0.8                     | −8.5                     | 22.1                        | 22.1                        | 2.7                        |
| JX-20-4    | Siliceous bands in dolomite (with bitumen) | Yangzhuang Fm., Jixian System | 1400     | −0.6                     | −7.6                     | 23.0                        | 22.9                        | 2.5                        |

Continued
| Sample No. | Sample type                                      | Strata                        | Age (Ma) | CaMg (CO₃)₂ | δ¹³C_PDB (‰) | δ¹⁸O_PDB (‰) | δ¹⁸O_SMOW (‰) | δ¹⁸O_SMOW (‰) | δ³⁰Si_NBS-28 (‰) | SiO₂ (%) |
|------------|-------------------------------------------------|-------------------------------|----------|--------------|---------------|---------------|---------------|---------------|-----------------|----------|
| IX-20-2    | Siliceous bands in dolomite (with bitumen)      | Yangzhuang Fm., Jixian System | 1400     | -1.4         | -8.8          | 21.8          | 23.1          | 2.8            |                 |
| IX-19      | Siliceous bands in dolomite                     | 4th member, Gaoyuzhuang Fm., Changcheng System | 1410     | -0.5         | -6.0          | 24.7          | 25.9          | 1.8            |                 |
| IX-10      | Siliceous bands in dolomite                     | 2nd member, Gaoyuzhuang Fm., Changcheng System | 1520     | -0.6         | -3.5          | 27.2          | 27.4          | 1.0            |                 |
| IX-09      | Black siliceous bands                           | 2nd member, Gaoyuzhuang Fm., Changcheng System | 1540     | -0.7         | -6.9          | 23.7          | 27.7          | 0.6            |                 |
| IX-05      | Siliceous bands in dolomite                     | 2nd member, Gaoyuzhuang Fm., Changcheng System | 1580     | 0.5          | -4.9          | 25.8          | 23.5          | 1.4            |                 |
| IX-04      | Siliceous stromatolite                          | Gaoyuzhuang Fm., Changcheng System | 1600     | 0.3          | -6.9          | 23.7          | 24.2          | 1.1            |                 |
| IX-75      | Dike of siliceous stromatolite                  | Dahongyu Fm., Changcheng System | 1610     |              |               |               | 22.4          | 0.6            |                 |
| IX-74      | Siliceous stromatolites                         | Dahongyu Fm., Changcheng System | 1620     |              |               |               | 25.8          | 0.5            |                 |
| IX-73      | Siliceous stromatolites                         | Dahongyu Fm., Changcheng System | 1625     |              |               |               | 24.7          | 0.7            |                 |
| IX-71      | Laminated chert                                 | Dahongyu Fm., Changcheng System | 1628     |              |               |               | 25.2          | 0.9            |                 |
| IX-70      | Siliceous band                                  | Dahongyu Fm., Changcheng System | 1630     |              |               |               | 25.1          | 0.5            |                 |

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It is known that the O isotope composition of silica would be reduced during diagenesis due to two factors. First, the chert nodular and band in the limestone are considered to form in the groundwater of mixed meteoric-marine coastal systems during diagenesis. Due to the involvement of meteoric water, the O isotope composition of groundwater would be lighter than that of contemporary marine water, causing a reduction in the 

 marine water, the relationship between the \( \delta^{18}O \) and \( \delta^{30}Si \) values of chert and those of the amorphous silica precursor must be evaluated first.

### Table 1

| Sample No. | Sample type               | Strata                                  | Age (Ma) | \( \delta^{13}C_{\text{VPDB}} \) (‰) | \( \delta^{18}O_{\text{VPDB}} \) (‰) | \( \delta^{18}O_{\text{VSMOW}} \) (‰) | \( \delta^{18}O_{\text{VSMOW}} \) (‰) | \( \delta^{30}Si_{\text{NBS-28}} \) (‰) |
|------------|---------------------------|-----------------------------------------|----------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|
| SSL-16     | Chert band                | 4th Member, Gaoyuzhuang Fm., Changcheng System | 1440     | -0.3                                | -5.3                                | 25.4                                | 17.6                                | 1.2                                 |
| SSL-18     | Siliceous stromatolite    | 4th Member, Gaoyuzhuang Fm., Changcheng System | 1410     | -0.4                                | -4.4                                | 26.3                                | 24.0                                | 2.4                                 |
| SSL-19     | Red chert rocks in Dol    | Yanghuang Fm., Jixian System             | 1400     | -0.7                                | -6.7                                | 24.1                                | 24.6                                | 2.4                                 |
| SSL-20     | Green chert band in Dol   | Yanghuang Fm., Jixian System             | 1390     | -1.4                                | -3.6                                | 27.2                                | 25.0                                | 2.4                                 |
| SSL-21     | Grey siliceous nodule     | Yanghuang Fm., Jixian System             | 1380     | -2.3                                | -3.7                                | 27.0                                | 24.5                                | 2.7                                 |
| SSL-22     | Massive chert             | 1st Member, Wumishan Fm., Jixian System   | 1375     | -0.1                                | -4.7                                | 26.0                                | 23.0                                | 1.6                                 |
| SSL-23     | Chert lenses              | 2nd Member, Wumishan Fm., Jixian System   | 1355     | -0.2                                | -5.0                                | 25.7                                | 20.9                                | 2.7                                 |
| SSL-24     | Banded chert rocks        | 2nd Member, Wumishan Fm., Jixian System   | 1330     | -0.3                                | -5.8                                | 24.9                                | 24.3                                | 2.2                                 |
| SSL-25     | Fine banded chert rocks   | 2nd Member, Wumishan Fm., Jixian System   | 1320     | -0.6                                | -5.3                                | 25.4                                | 22.5                                | 1.9                                 |
| SSL-26     | White-grey chert rocks    | 2nd Member, Wumishan Fm., Jixian System   | 1310     | -0.9                                | -7.2                                | 23.4                                | 25.8                                | 2.1                                 |
| SSL-27     | Silica-bearing brecciate Dol | 3rd Member, Wumishan Fm., Jixian System | 1300     | 0.4                                 | -5.6                                | 25.1                                | 22.6                                | 2.5                                 |
| SSL-28     | Siliceous nodule in Dol   | 3rd Member, Wumishan Fm., Jixian System   | 1290     | 0.6                                 | -5.2                                | 25.5                                | 19.3                                | 2.1                                 |
| SSL-29     | White-grey quartzite      | 3rd Member, Wumishan Fm., Jixian System   | 1280     | -0.9                                | -3.9                                | 26.8                                | 20.6                                | 2.6                                 |
| SSL-30     | Black-grey siliceous Dol  | 3rd Member, Wumishan Fm., Jixian System   | 1270     | -1.1                                | -4.8                                | 25.9                                | 16.9                                | 2.2                                 |
| SSL-31     | Black-grey siliceous nodule | 3rd Member, Wumishan Fm., Jixian System | 1260     | -0.8                                | -4.3                                | 26.4                                | 16.6                                | 2.0                                 |
| SSL-32     | Black-grey siliceous band | 4th Member, Wumishan Fm., Jixian System   | 1250     | -0.1                                | -4.6                                | 26.1                                | 14.1                                | 1.1                                 |
| SSL-33     | Siliceous stromatolite    | 4th Member, Wumishan Fm., Jixian System   | 1240     | -0.2                                | -4.8                                | 25.9                                | 25.5                                | 3.4                                 |
| SSL-34     | Siliceous nodule in white-grey Dol | 4th Member, Wumishan Fm., Jixian System | 1230     | 0.3                                 | -4.1                                | 26.6                                | 15.7                                | 1.8                                 |
| SSL-35     | Black chert band in white-grey Dol | 4th Member, Wumishan Fm., Jixian System | 1220     | 0.2                                 | -3.8                                | 26.9                                | 16.1                                | 1.7                                 |
| SSL-37     | Chert band in grey Dol    | 4th Member, Wumishan Fm., Jixian System   | 1200     | 1.2                                 | -5.4                                | 25.3                                | 17.4                                | 1.7                                 |
δ¹⁸O value of chert to some extent. Second, as the diagenetic temperature is normally higher than that of marine water, the O isotope fractionation between silica and water at the diagenetic stage would be smaller than that in the precipitation stage, which would cause a δ¹⁸O reduction in the chert. As shown by the microscopic and SEM examinations (Fig. 3), the slight reduction in the δ¹⁸O value of chert indicates that the studied cherts were formed in the diagenetic process and their δ¹⁸O values cannot represent those of the amorphous silica precursor.

In contrast to the O isotope composition, the silicon isotope composition would not change during early diagenesis for following reasons: (1) Chert bands and nodules are commonly confined in layers of sedimentary strata, which indicate that silica does not move over long distances during diagenesis. (2) The amorphous silica precursor is the dominant form of silica in dolomite rocks and the Si content in groundwater is rather limited. (3) δ³⁰Si variations at the millimetre scale or even the micrometre scale³,⁸,¹³,¹⁴,³²,³³ are preserved in cherts, which rules out the possibility of the large-scale mixing of silicon during diagenesis. Thus, the δ³⁰Si value of chert can be used as a representative of the amorphous silica precursor to trace the silicon isotope composition of contemporary seawater⁵.

In Fig. 5, the inferred variation trend in δ³⁰SiSW (δ³⁰Si value of seawater) is shown. The δ³⁰SiSW is calculated from δ³⁰SiCh.

![Figure 4.](image1)

Figure 4. The temporal evolution of δ³⁰SiNBS-28 and δ¹⁸O_V-AMOW values of chert and δ¹³C_V-PDB and δ¹⁸O_V-PDB values of dolomite for the samples collected in this study. Analytical precisions are provided in Table 1.

![Figure 5.](image2)

Figure 5. A plot showing δ³⁰Si variations of chert formed in a shallow marine environment, and inferred ocean water, from the late Archean to the present. Previous data for Proterozoic chert (Pt)¹⁰,²⁴–⁵⁸ and Phanerozoic chert (Pn)²,²⁴,²⁷–⁵⁸ are included. Taking Δ³⁰SiCh-SW to be −0.5‰, −1.0‰ and −1.2‰ in the Archean, early Proterozoic and since the middle Proterozoic, respectively, δ³⁰SiSW values are calculated from δ³⁰SiCh.
relative Si isotope enrichment of chert to seawater. According to the theory of isotope fractionation, $\Delta^{30}Si_{\text{Ch-SW}}$ is temperature dependent. Thus, to determine a proper $\Delta^{30}Si_{\text{Ch-SW}}$ value, precipitation temperatures of the amorphous silica precursor of chert should be evaluated beforehand.

Based on the O isotope composition of chert, Robert and Chaussidon (2006)3 suggested the seawater temperatures were 70 °C at 3.5 Ga and 35 °C at 0.85 Ga. However, the inferred high Paleoarchean temperatures are controversial4–8, partly because $\delta^{18}O$ determinations of the Paleooarchean temperature rely on the assumption that $\delta^{18}O$ of the Archean ocean was similar to that of an ice-free modern ocean. However, it has been suggested by a number of researchers that the $\delta^{18}O$ value of the global ocean could have varied significantly over time9–18. Recently Hren et al.34 studied the $\delta^{18}O$ and $\delta$D values of the 3.42 Ga Buck Reef Chert rocks in South Africa and found that the chert with the highest $\delta^{18}O$ was formed in equilibrium with waters below 40°C. Blake et al. (2010) studied the oxygen isotope composition of phosphate in 3.2–3.5 Ga sediments of the Barberton Greenstone Belt and found that the phosphate with the highest $\delta^{34}S$ value was formed in seawater at a temperature range from 26°C to 35°C. According to these results, a temperature range of 35°C–40°C is more acceptable for the Archean ocean.

For the temperature of the Proterozoic ocean, fewer results have been reported. Based on the O isotope composition of chert, the temperatures in the Proterozoic ocean are estimated in the range of 35–60 °C3. According to the $\delta^{18}O$ values of chert and dolomite obtained in this study, the diagenetic temperature can be estimated. Assuming that diagenetic water has a $\delta^{18}O$ value of −10‰, and using the O isotope fractionation equation ($1000\ln(\rho_{\text{dol}}/\rho_{\text{HDO}}) = 3.20 \times 10^6 T^{-2} - 2.0$) of Northrop and Clayton (1966)19, we obtained a diagenetic temperature range of 25–36 °C (averaging 36 ± 7°C) for dolomite in the early Proterozoic and a diagenetic temperature range of 12–20 °C (averaging 26 ± 9°C) for dolomite in the middle Proterozoic. Assuming the diagenetic water still has a $\delta^{18}O$ value of −10‰, and using the O isotope fractionation equation ($1000\ln(\rho_{\text{dol}}/\rho_{\text{HDO}}) = 3.09 \times 10^6 T^{-2} - 2.29$) of Knauth & Epstein (1975), we obtained a diagenetic temperature range of 19–43 °C (averaging 34 ± 7°C) for chert in the early Proterozoic and 1–63 °C (averaging 17 ± 15°C) for chert in the middle Proterozoic. The calculated average diagenetic temperature (34°C) for early Proterozoic chert is slightly lower than that (36°C) for early Proterozoic dolomite, and the calculated average diagenetic temperature (17°C) for middle Proterozoic chert is significantly lower than that (26°C) for middle Proterozoic dolomite. These observations may be caused by a difference between chert and dolomite during O isotope exchange process with diagenetic solution. The cherts are more resistant to O isotope exchange than dolomite in the diagenetic process. Thus, the calculated diagenetic temperature for dolomite may be more representative. Based on these considerations and assuming the diagenetic temperature is a little higher than the sedimentary temperature on the sea floor, we estimate the ocean temperature as 30°C in the early Proterozoic and 20°C in the middle Proterozoic.

Concerning $\Delta^{30}Si_{\text{Ch-SW}}$, there has been a number of investigations on Si isotope fractionation during abiotic silica precipitation15–17,24,42–45. Early experimental studies on abiotic solid–fluid silicon isotope fractionation yielded $\Delta^{30}Si_{\text{solid-fluid}}$ values ranging from −2.0‰ to −1.0‰42,44. Geilert et al. (2014) performed seeded silica precipitation experiments using flow-through reactors in the 10–60 °C temperature range to quantify the silicon isotope fractionations during controlled precipitation of amorphous silica from a flowing aqueous solution15. The obtained $\Delta^{30}Si_{\text{silica-solution}}$ values were −2.1‰ at 10 °C, −1.2‰ at 20 °C, −1.0‰ at 30 °C, −0.5‰ at 40 °C, 0.1‰ at 50°C, and 0.2‰ at 60°C. These results can be used to calculate $\delta^{30}Si$ values of ocean water in different geological periods.

Assuming that the temperature of the ocean is 40°C, 30°C and 20°C in the Archean, early Proterozoic and since the middle Proterozoic, respectively, and $\Delta^{30}Si_{\text{Ch-SW}}$ are −0.5‰, −1.0‰ and −1.2‰ in the Archean, early Proterozoic and since the middle Proterozoic, respectively, $\delta^{30}Si$ values of ocean water are calculated from $\delta^{30}Si$ values of chert (Fig. 5).

Figure 5 shows that the upper limit of inferred $\delta^{30}Si_{\text{NBS-28}}$ values in ocean water increases gradually from 2.8‰ at 2.53 Ga to 5.1‰ at 1.335 Ga and then decreases drastically to 3.2‰ at 1.104 Ga. After 1.104 Ga, the upper limit of inferred $\delta^{30}Si_{\text{NBS-28}}$ values in ocean water fluctuates between 2.7‰ and 3.7‰.

As shown in Fig. 6, during the Archean period, the input sources of dissolved Si to the ocean are submarine hydrothermal fluid and sea-floor weathering, and the output paths are chemical precipitation (to form C cherts) and silification of the precursor sediments or rocks (to form S cherts)4–6. The Si concentration in ocean water remains in its saturated concentration at a given temperature, but the $\delta^{30}Si_{\text{SW}}$ increases gradually due to Si isotope fractionation between dissolved Si and precipitated SiO$_2$. When a steady state is reached, $\delta^{30}Si_{\text{SW}}$ (the average $\delta^{30}Si$ value of all output Si) will be equivalent to $\delta^{30}Si_{\text{Input}}$ (the average $\delta^{30}Si$ value of input Si), and $\delta^{30}Si_{\text{SW}}$ will be equal to $(\delta^{30}Si_{\text{Input}} - \Delta^{30}Si_{\text{out-SW}})$, where $\Delta^{30}Si_{\text{out-SW}}$ is the relative silicon isotope enrichment of the output Si to the ocean water ($\delta^{30}Si_{\text{out-SW}} - \delta^{30}Si_{\text{SW}}$). Because the average $\delta^{30}Si$ value of Si in the submarine hydrothermal fluid and Si from sea-floor weathering is ~−0.3‰ and $\Delta^{30}Si_{\text{out-SW}}$ is ~−0.5‰ at a temperature of 40°C17, the $\delta^{30}Si_{\text{SW}}$ value of that period is approximately 0.2‰.

The Si cycle in the modern ocean (Fig. 6) is quite different46. First, dissolved Si from the continents (in rivers7 and groundwater) has become a dominant input source (6.4 Tmol Si/a) to ocean Si, and the Si input from submarine hydrothermal fluid (0.6 Tmol Si/a) and sea-floor weathering (1.9 Tmol Si/a) has become less significant46. $\delta^{30}Si_{\text{SW}}$ is calculated as −0.78‰ using the equation

$$\delta^{30}Si_{\text{SW}} = f_{\text{Cont}} \delta^{30}Si_{\text{Cont}} + f_{\text{SFW}} \times \delta^{30}Si_{\text{SFW}} + f_{\text{SHF}} \times \delta^{30}Si_{\text{SHF}}.$$  (2)

In the equation, f represents the relative fraction of each Si source and the subscripts Cont, SFW and SHF indicate continent, sea-floor weathering and submarine hydrothermal fluid, respectively.

Second, the biological absorption of Si has become a dominant path for Si output from the ocean and Si contents in modern ocean water (0.05 mg/L–0.2 mg/L for shallow seawater and 0.3 mg/L–3.5 mg/L for deep seawater) are 2 orders of magnitude lower than those of the saturated concentration in seawater7. At steady state, the
amount and δ^{30}Si value of output Si from ocean water would be equal to those of input Si. Thus, δ^{30}Si_{Out} would also be ~0.78‰ at present.

The silicon isotope fractionations of diatoms-seawater and sponges-seawater have been experimentally studied. The determined Δ^{30}Si_{Diatom-SW} is commonly −1.0∼−1.1‰48–50, but Δ^{30}Si_{Sponge-SW} varies from −1.1‰ to −3.7‰51,52. Because diatoms are much more abundant in the ocean than sponges, we assume Δ^{30}Si_{Out-SW} in the modern ocean is ~−1.2‰. From the above estimation, the δ^{30}Si_{SW} value of the modern ocean can be calculated as ~1.98‰, which is very close to the value (1.9‰) of surface ocean water inferred previously53.

Many papers have reported the δ^{30}Si values of cherts formed during the Proterozoic1–3,8–10,24–26,32, but no model of the Si cycle in the Proterozoic ocean has been presented. Here, we present a conceptual model for the Si cycle of the Proterozoic ocean based on known and inferred boundary conditions (Fig. 6). Similar to the conditions in the Archean ocean, submarine hydrothermal fluid and sea-floor weathering are still important input sources of dissolved Si to the Proterozoic ocean, but the amounts of these inputs decreased as the hydrothermal activity and ocean temperature decreased from their Archean to Proterozoic values. Further, the input of dissolved Si from the continents became significant as supercontinents appeared in the early Proterozoic. For the output of dissolved Si from the ocean in the Proterozoic Eon54, chemical precipitation was still a major pathway, but biological absorption may have also played a significant role.

The Si concentration in ocean water remains in its saturated concentration at a given temperature (30 °C for the early Proterozoic and 20 °C for the middle and late Proterozoic). When a steady state is reached, δ^{30}Si_{Out} will be equivalent to δ^{30}Si_{In}, and δ^{30}Si_{SW} will be equal to δ^{30}Si_{Out-SW}, where Δ^{30}Si_{Out-SW} is ~−1.0‰ for the early Proterozoic and −1.2‰ for the middle and late Proterozoic. The estimated δ^{30}Si_{SW} value of that period would be approximately 1.47‰ (Fig. 6).

From the discussion above, extreme values of δ^{30}Si for chert and δ^{30}Si for seawater cannot be explained for an ocean at steady state conditions. Thus, this peak in δ^{30}Si indicates an extraordinary period at non-steady state suggesting a scenario at a transition stage.

From the Archean to present, there should be a transition period of the Si cycle in the ocean. In that period, the D_{Si} in ocean water is reduced by approximately 2 orders of magnitude below that of the saturated concentration in seawater, and the δ^{30}Si_{SW} value first rises from ~0.2‰ to ~5.1‰ and then decreases to ~1.98‰. The rise of δ^{30}Si_{SW} is caused by Rayleigh fractionation when SiO_{2} precipitates from ocean water (Fig. 7). One mechanism that causes the D_{Si} reduction in ocean water should be a decrease in ocean temperature. As temperature decreases, the saturated Si concentration in ocean water would be reduced, causing additional SiO_{2} precipitation.

Figure 6. A schematic diagram showing Si cycles in the Archean4–6, Proterozoic and modern oceans29.
The saturated SiO₂ concentration in ocean water is ~363.5 mg/L, ~221.2 mg/L and ~178.9 mg/L at 40 °C, 30 °C and 20 °C, respectively. When the temperature of seawater decreases from 40 °C to 20 °C, the fraction of dissolved Si remaining in the seawater (f) will be reduced to ~0.687. In the Rayleigh fractionation process, it will cause an increase of ~0.2‰ in $\delta^{30}$Si$_{SW}$. It seems that the decrease in seawater temperature alone cannot explain the significant increase in the $\delta^{30}$Si$_{SW}$ value, and other mechanisms should be considered. Another mechanism causing a DSi decrease in ocean water is the increase of Si absorption activities by biological species, which can reduce the DSi in ocean water 2 orders of magnitude lower than that of the saturated concentration. In the Rayleigh fractionation process, the combined effect of these two types of mechanisms can cause $\delta^{30}$Si$_{SW}$ to increase ~4.0‰ when f is reduced to 0.01. It is known that diatoms and radiolarians are Si-fixing organisms that were active in the Phanerozoic; sponges were active in the Phanerozoic and the later Proterozoic. Assuming their appearance is the start of a drastic decrease of DSi in ocean water, we should observe a $\delta^{30}$Si$_{SW}$ peak value in the later Proterozoic or early Phanerozoic. However, according to the data here, the $\delta^{30}$Si$_{SW}$ peak appeared in the middle Proterozoic (1.325–1.355 Ga) instead, which indicates the drastic decrease in ocean water DSi happened prior to 1.355 Ga.

It is known that microbes were the dominant biological species in the Precambrian. Stromatolites are found in early Archean strata from 3.5 Ga and are very well developed in Proterozoic strata. REE and C, O, Nd isotope compositions have been used to study the formation conditions of stromatolite-bearing sediments, particularly the effect of biological activities. The early and middle Proterozoic chert-bearing dolomites investigated in this study are all rich in stromatolites, showing a close correlation between silica precipitation and biological activities. Moreover, macroscopic eukaryotic fossils were recently discovered in the 1.56 Ga Gaoyuzhuang Formation in the Yanshan area of Northern China. If some Proterozoic species are capable of absorbing or precipitating Si from ocean water, the Si content in the Proterozoic ocean water would be drastically reduced causing $\delta^{30}$Si$_{SW}$ to rise significantly. Thus, the high peak in $\delta^{30}$Si$_{SW}$ values in the middle Proterozoic ocean water may reflect a drastic reduction in Si content caused by a rapid increase in biological activity in the ocean. After that peak period, the DSi reduction rate in ocean water decreased gradually, and the $\delta^{30}$Si$_{SW}$ value decreases to a significantly lower value at steady state.

**Methods**

**Si and O isotope analysis of chert samples.** For Si and O isotope analysis, ~100 mg of a chert band or nodule was selected from a polished section of each specimen. The sample was crushed and ground to a powder of ~200 mesh. Then, the sample powder was reacted with 6 N HCl in Teflon beakers to dissolve small amounts of carbonate. The remainder was washed at least in triplicate with Milli-Q water. Then, the remainder was transferred to a Pt crucible, dried at 105 °C in an oven and then calcined at 1000 °C in a muffle furnace to remove organic C impurities.
Oxygen isotope analyses were carried out using the BrF₅ method (Clayton and Mayeda, 1963)⁶⁰, and silicon isotope analyses were carried out using the SiF₄ method (Ding, 2004)⁶¹. Approximately 10 mg of pretreated chert was placed in a Ni reactor in a metal vacuum line and reacted with BrF₅ at a temperature of approximately 500°C to produce gaseous O₂ and SiF₄. The O₂ gas was separated from SiF₄, BrF₅ and BrF₃ by evaporating at liquid nitrogen temperature. Then, O₂ gas was converted to CO₂ by reacting with a carbon rod at 700°C. Finally, the CO₂ gas was collected for O₂ isotope measurement.

SiF₄ was separated from the BrF₅ and BrF₃ by evaporating at dry ice-acetone temperature. The separated SiF₄ was purified further by passing it through a Cu tube containing pure Zn particles at a temperature of 60°C. This procedure removed trace amounts of the remaining active F-bearing compounds (BrF₅ and BrF₃). Then, the purified SiF₄ was collected for silicon isotope measurement.

The isotopic measurements were carried out with a MAT-253 mass spectrometer. For O₂ isotope measurement, the NIST Standard Reference Material for O isotopes (NBS-28) was used directly as the working standard in this study. The precision of the O isotope measurement is better than ± 0.2‰ (2σ). The O isotope compositions of all samples are reported as δ¹⁸O values relative to the V-SMOW standard.

For Si isotope measurements, international reference material for Si isotopes (NBS-28) and two Chinese national standards for Si isotopes (GBW04421 and 04422) were used as working standards in this study. The long-term reproducibility of the silicon isotope measurements is better than ± 0.1‰ (2σ). The silicon isotope compositions of all samples are reported as δ³⁰Si values relative to the NBS-28 standard.

C and O isotope analysis of dolomite samples. The continuous-flow isotope-ratio mass spectrometric method was used for C and O isotope analysis of dolomite⁶². The system consists of a Thermo-Finnigan GasBench II equipped with a CTC Combi-Pal auto-sampler and linked to a Finnigan MAT 253 mass spectrometer.

Approximately 100 mg of dolomite was taken from the specimen and ground to a powder of ~200 mesh. Approximately 100μg of dolomite powder was loaded manually into a 12 ml round-bottomed borosilicate exeterant and sealed using butyl rubber septa. Four national reference materials (GBW04405, GBW04406, GBW04416 and GBW04417) were routinely loaded. The exetainers were automatically flushed with grade 5 He by penetrating the septa using a double-hole needle at a flow rate of 100 mL/min. Then, 4–6 drops of phosphoric acid were deposited in each exetainer. The exetainers were placed onto an aluminium tray and kept at 72°C for 24 h. Subsequently, the sample gas was introduced into the mass spectrometer through the standard 100μL sample loop. CO₂ was separated from other components using a gas chromatographic column heated to 70°C, and the peak corresponding to this CO₂ was passed via an open split to the mass spectrometer.

The calculated external precision is typically ± 0.2‰ (2σ) for δ¹³C and δ¹⁸O. The C isotope compositions of the dolomite samples are reported as δ¹³C values relative to the V-PDB standard. The O isotope compositions of the dolomite samples are reported as δ¹⁸O values relative to V-PDB and V-SMOW standards.

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**Author Contributions**

T. P. Ding designed the research and wrote the manuscript. J. F. Gao, S. H. Tian and Y. Zhao are responsible for sample collection and treatment. D. F. Wan and C. F. Fan completed the analytical work for the Si, O and C isotopes. J. X. Zhou completed the SEM analysis of chert.

**Additional Information**

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