

increases and diminishes at ~ 10 K, suggesting a relation to Tb magnetic ordering. At 28 K, ϵ exhibits a field-induced 'step' anomaly with a larger hysteresis rather than a peak, consistent with the H dependence of the step feature in $\epsilon(T)$ shown in Fig. 2a as well as $P(H)$ in Fig. 3b.

The electric polarization shows a startling magnetic-field-induced reversal at low T , shown in Fig. 3b. At 3 K, the direction of P is completely reversed with a rather low H , corresponding to a change in P of ~ 80 nC cm $^{-2}$ at 2 T. This change in P for H below 2 T is considerably large and nonlinear, suggesting that this behaviour stems from H -induced phase transitions^{16,17}, possibly associated with the H -induced change of Tb magnetism. However, the P change for high H is rather linear with H , indicating that the linear magnetoelectric effect^{14,27} becomes active above 2 T. These results are certainly consistent with the behaviour of magnetization, which saturates for H along the a axis above 2 T. Note that the magnetic symmetry $P_{2a}m'c'2_1$ (magnetic point group, $m'm'2$) in zero field proposed from a neutron diffraction study^{18,22} allows only non-zero diagonal elements of the linear magnetoelectric tensor^{14,15}, but H along the a axis above 2 T appears to induce ferromagnetic Tb ordering, changing the magnetic symmetry and thus allowing a large off-diagonal linear magnetoelectric coefficient, α_{21} , of about -21 ps m $^{-1}$. We also point out that the reversible P flip along the $\pm b$ axis with $H = 0-2$ T should be distinguished from the non-reversible 180° switching of the spontaneous polarization induced by the 90° rotation of magnetic field in Ni $_3$ B $_7$ O $_{13}$ I (ref. 6), the non-reversible 180° switching of the spontaneous polarization of a portion of the ferroelectric domains in Tb $_2$ (MoO $_4$) $_3$ (ref. 11), and the 90° rotation of P by applied $H \approx 5$ T in TbMnO $_3$ (ref. 12).

We performed a sequential flipping of P by slowly varying H linearly from 0 to 2 T. A strikingly reversible and reproducible variation of the polarization was observed without any noticeable decay in its magnitude, as displayed in Fig. 3c. By combining this highly reproducible P reversal with the ability to leave a permanent 'imprint' in the polarization with an applied magnetic field demonstrated in Fig. 3c and Fig. 2d, respectively, one can envision a ferroelectric memory that can be magnetically recorded. □

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Evidence from massive siderite beds for a CO $_2$ -rich atmosphere before ~ 1.8 billion years ago

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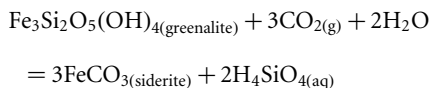
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It is generally thought that, in order to compensate for lower solar flux and maintain liquid oceans on the early Earth, methane must have been an important greenhouse gas before ~ 2.2 billion years (Gyr) ago^{1–5}. This is based upon a simple thermodynamic calculation that relates the absence of siderite (FeCO $_3$) in some pre-2.2-Gyr palaeosols to atmospheric CO $_2$ concentrations that would have been too low to have provided the necessary greenhouse effect¹. Using multi-dimensional thermodynamic analyses and geological evidence, we show here that the absence of siderite in palaeosols does not constrain atmospheric CO $_2$ concentrations. Siderite is absent in many palaeosols (both pre- and post-2.2-Gyr in age) because the O $_2$ concentrations and pH conditions in well-aerated soils have favoured the formation of ferric (Fe $^{3+}$)-rich minerals, such as goethite, rather than siderite. Siderite, however, has formed throughout geological history in subsurface environments, such as euxinic seas, where anaerobic organisms created H $_2$ -rich conditions. The abundance of large, massive siderite-rich beds in pre-1.8-Gyr sedimentary sequences and their carbon isotope ratios indicate that the atmospheric CO $_2$ concentration was more than 100 times greater than today, causing the rain and ocean waters to be more acidic than today. We therefore conclude that CO $_2$ alone (without a significant contribution from methane) could have provided the necessary greenhouse effect to maintain liquid oceans on the early Earth.

The current popular model of a methane-rich Archaean atmosphere was first proposed by Rye *et al.*¹, who suggested that pre-2.2-Gyr palaeosols were characterized by the absence of iron-bearing minerals in the upper parts and by the presence of chlorite (a Fe $^{2+}$ - and Fe $^{3+}$ -rich aluminous silicate) in the lower parts of soil sections. They assumed that the precursor of chlorite before metamorphism

was greenalite (a Fe^{2+} -silicate) and that the Fe^{2+} leached by rain water from the upper soil section precipitated greenalite, not siderite (a Fe^{2+} -carbonate), in the lower soil section. Rye *et al.*¹ evaluated the stability relation of greenalite and siderite from the following reaction:



The stability relation of the two minerals at a given temperature and pressure condition depends on only two parameters: the partial pressure of gaseous CO_2 and the concentration of aqueous silica in solution. Using thermodynamic data from the literature, Rye *et al.*¹ calculated that greenalite, not siderite, becomes stable at $p_{\text{CO}_2} < 10^{-2.2}$ atm at 10°C (and $< 10^{-1.7}$ atm at 30°C) when $\text{H}_4\text{SiO}_4(\text{aq})$ is between $\sim 10^{-4}$ and $\sim 10^{-3.4}$ *m* (where *m* is concentration in moles per kg H_2O) (that is, ~ 6 to ~ 24 p.p.m. $\text{SiO}_2(\text{aq})$, a typical range in groundwater). By further assuming soil p_{CO_2} values were between $\sim 60\%$ and 100% of the atmospheric p_{CO_2} , they concluded that the maximum p_{CO_2} in the pre-2.2-Gyr atmosphere was $\sim 10^{-1.4}$ atm.

This maximum p_{CO_2} value is, however, less than the 'best guess' p_{CO_2} values (for example, $\sim 10^{-0.7}$ atm at 2.75 Gyr) estimated by Kasting⁶ from a one-dimensional climatic model where the primary greenhouse gas was CO_2 (curve $\text{CO}_2(\text{K})$ in Fig. 1). Because of this p_{CO_2} discrepancy, Rye *et al.*¹ suggested that another greenhouse gas, most probably methane, was important in the pre-2.2-Gyr atmosphere. Subsequently, a revised climatic model^{4,5} suggests values of $\sim 1,000$ p.p.m. ($\sim 10^{-3}$ atm) CH_4 and $\sim 2,500$ p.p.m. ($\sim 10^{-2.6}$ atm) CO_2 for the atmosphere at 2.8 Gyr ago (curves $\text{CO}_2(\text{P})$ and $\text{CH}_4(\text{P})$ in Fig. 1). For comparison, today's atmosphere contains only ~ 1 p.p.m. ($\sim 10^{-6}$ atm) CH_4 and ~ 350 p.p.m. ($\sim 10^{-3.5}$ atm) CO_2 (Fig. 1). Here we show a serious flaw in the thermodynamic approach by Rye *et al.*¹, which led to the suggestion of a methane-rich Archaean atmosphere²⁻⁵.

Rye *et al.*¹ neglected two important facts: (1) the formation of siderite (and any other Fe-bearing minerals) depends not only on p_{CO_2} and $m\text{H}_4\text{SiO}_4(\text{aq})$, but also on additional geochemical parameters, including p_{O_2} , pH and concentrations of Fe^{2+} species in solution; and (2) siderite is a very abundant mineral in pre-1.8-Gyr sedimentary rocks, especially in banded iron formations (BIFs). For example, Fig. 2a illustrates that the formation of a Fe^{2+} -rich mineral (for example, greenalite, minnesotaite, fayalite, annite or siderite) requires an extremely low p_{O_2} condition ($< 10^{-6.5 \pm 5}$ atm). Many researchers agree that the atmospheric p_{O_2} was much greater than $\sim 10^{-60}$ atm throughout geologic history, although suggested values vary greatly: for example, $\sim 10^{-13}$ atm (ref. 6), $\sim 10^{-4}$ atm (ref. 2) and ~ 0.2 atm (ref. 7) at ~ 2.75 Gyr ago (Fig. 2a). Soil p_{O_2} values are

typically less than the atmospheric p_{O_2} value owing to reactions with Fe^{2+} -bearing minerals and organic matter, but generally remain $\geq 10^{-60}$ atm in well-aerated soils⁸ (see Methods). At $p_{\text{O}_2} \geq 10^{-60}$ atm, siderite (or any ferrous-rich mineral) becomes unstable regardless of the p_{CO_2} value; instead, ferric-rich minerals, such as goethite (FeOOH), become stable (Fig. 2a).

Goethite transforms to haematite (Fe_2O_3) at temperatures $\geq 80^\circ\text{C}$ owing to dehydration⁸. A thick haematite-enriched zone, which was most probably a goethite-enriched zone before regional metamorphism, has been recognized in the upper parts of the ~ 2.3 -Gyr Ville Marie palaeosols⁹ in Canada, the ~ 2.3 -Gyr Hakkalampi palaeosols¹⁰ in Finland and the ~ 2.2 -Gyr Hekpoort palaeosols¹¹ in South Africa. The chlorite in a lower part of the Hekpoort palaeosols is a Fe^{3+} -rich aluminous silicate¹⁰, not pure Fe^{2+} silicate as assumed by Rye *et al.*¹. Furthermore, ferri-stilpnomelane (another Fe^{3+} -rich aluminous silicate) is abundant in the uppermost part of the 2.6-Gyr Schagen palaeosol¹². Many palaeosols have lost the uppermost parts through erosion during the deposition of overlying rock units, but the remaining soil profiles have retained the original characteristics of Fe^{3+} enrichments from the parental values⁷. (Although some earlier researchers wondered whether the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios of Precambrian palaeosols were increased by modern weathering, recent investigators have concluded that many palaeosol sections have retained the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios of original palaeosols^{2,7,10,11}). Therefore, both the thermodynamic predictions and natural examples clearly indicate that goethite and Fe^{3+} -rich aluminous silicates were stable minerals during soil formation both before and after 2.2 Gyr ago. The absence of siderite in the pre-2.2-Gyr soils that were investigated by Rye *et al.*¹ and in many younger palaeosols was not because the atmospheric p_{CO_2} was $< 10^{-1.4}$ atm as they suggested, but because the p_{O_2} values in well-aerated soils were typically much greater than $10^{-65 \pm 5}$ atm (Fig. 2a; Methods). In fact, Fe-rich carbonates formed in the ~ 2.6 -Gyr Schagen palaeosols¹² during periods when the soils were submerged in a shallow water body (pond or lake) where anaerobes created anoxic conditions (see Methods).

Another reason for the absence of siderite in well-aerated soils, both before and after 2.2 Gyr ago, is that siderite is only stable at pH conditions of more than ~ 1.5 units above the rainwater pH values (Fig. 2b). However, increases in soil pore-fluid pH (due to reactions with minerals) are typically by less than ~ 1.5 units (ref. 8).

Although Fe^{2+} -rich carbonates (siderite, ankerite and ferroan dolomite) are rare in well-aerated soils and palaeosols, they are not uncommon in sedimentary rocks (marine and freshwater) of all geologic age. For siderite formation, all of the following conditions must be satisfied (Fig. 2): (1) a very low p_{O_2} ($\leq 10^{-60}$ atm); (2) a very high p_{CO_2} ($> 10^{-1.4 \pm 0.2}$ atm); (3) a slightly acidic to near-neutral pH (~ 5.5 to ~ 7.5); and (4) a high concentration of ΣFe^{2+} ($= \text{Fe}^{2+} + \text{FeHCO}_3^-$) in water, most probably within a range of ~ 0.1 to ~ 100 p.p.m. ($m\Sigma\text{Fe}^{2+} = \sim 10^{-6}$ to 10^{-3}), corresponding to the typical ΣFe^{2+} concentrations in low-temperature ($< 200^\circ\text{C}$) natural solutions⁸.

Archaean oceans may have been considerably warmer and much more silica-rich than today¹³ ($\text{SiO}_2(\text{aq}) = \sim 6$ p.p.m. today⁸). The p_{CO_2} value for the minnesotaite/siderite boundary, assuming a $\text{SiO}_2(\text{aq})$ concentration of 24 p.p.m., is $10^{-1.7}$, $10^{-1.6}$ and $10^{-1.3}$ atm at 10° , 25° and 50°C , respectively. However, if the $\text{SiO}_2(\text{aq})$ concentration of the Archaean oceans was as high as ~ 100 p.p.m., it becomes $10^{-1.2}$ atm at 25°C . Considering these variations, we propose here a p_{CO_2} value of $10^{-1.4 \pm 0.2}$ atm as the minimum p_{CO_2} requirement for siderite formation throughout geologic history. A combination of high p_{CO_2} and low pH creates carbonate-rich water with a ΣCO_3^{2-} ($\approx \text{CO}_2(\text{aq}) + \text{HCO}_3^-$) concentration between $\sim 10^{-2.5}$ and $\sim 10^{-0.5}$ *m* (compared with $\sim 10^{-3}$ *m* in today's open oceans⁸) (Fig. 2b). Subsurface waters (for example, lower water columns in euxinic seas; pore fluids in soils and sediments) may acquire all the necessary conditions for siderite

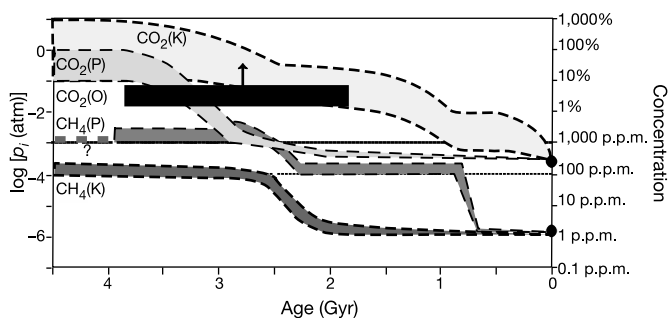


Figure 1 Proposed models for the evolution of atmospheric CO_2 and CH_4 . Curve $\text{CO}_2(\text{K})$ is reproduced from Kasting⁶; curve $\text{CH}_4(\text{K})$ was constructed from descriptions in Kasting⁶; curves $\text{CO}_2(\text{P})$ and $\text{CH}_4(\text{P})$ were constructed from the values estimated by Pavlov *et al.*^{4,5,27} at 3.9 Gyr, 2.8 Gyr and 2.3–0.75 Gyr ago; and line $\text{CO}_2(\text{O})$ is from this study. p_i refers to the partial pressure of a gaseous species *i*.

formation through a series of microbial and non-microbial reactions involving Fe-bearing minerals and organic matter (see Methods).

The major mechanism for siderite formation seems to have changed through geologic history, because distinct differences exist in the abundance, the occurrence and the chemical and isotopic compositions of siderite crystals between those younger and those older than ~ 1.8 Gyr. In post-1.8-Gyr sedimentary formations, Fe-rich carbonates rarely form massive beds but typically occur as disseminated crystals, cements and nodules in organic carbon-rich clastic sediments (mudstones and sandstones). The carbonate content is generally less than 10 vol.%, and the Fe/Ca ratios and $\delta^{13}\text{C}$ values are highly variable on the millimetre scale^{14,15}. These observations suggest that these siderite crystals formed during the diagenetic stage of host sediments, and that the necessary conditions for siderite formation were locally created for the pore fluids in organic carbon-rich sediments. In fact, the p_{O_2} - p_{CO_2} -pH conditions of subsurface waters with abundant anaerobes (for example, water-logged soils, euxinic lakes and seas) typically fall around the goethite-siderite boundary⁸ (Fig. 2a).

Many modern siderite crystals, especially those formed in sulphate-poor terrestrial environments (for example, ponds and lakes), possess very positive and variable $\delta^{13}\text{C}$ values (for example, $\sim +10\text{‰}$; Fig. 3a), suggesting the use of the ΣCO_3^{2-} generated from the decomposition of organic matter by methanogens^{14,15} (see reaction (6) in Methods). In contrast, siderite crystals that formed in sulphate-rich environments (for example, marine sediments) tend to possess negative and variable $\delta^{13}\text{C}$ values (Fig. 3b) owing to

the significant contribution of the ΣCO_3^{2-} generated from the decomposition of organic matter by non-methanogenic microbes, especially sulphate reducers¹⁵ (see reactions (1)–(5) in Methods).

In contrast to the siderite occurrences in young sediments, Fe-rich carbonates in many pre-1.8-Gyr sedimentary sequences formed massive beds of tens to hundreds of metres in thickness, and hundreds to thousands of thousands of square kilometres in aerial extent¹⁶. In fact, Fe-rich carbonates are more abundant than Fe-oxides (haematite and magnetite) in many BIFs that are mostly ~ 3.8 to ~ 1.8 Gyr in age¹⁶. Primarily on the basis of rare-earth-element characteristics, many investigators agree that the iron in BIFs was derived from oceanic basalts by submarine hydrothermal fluids^{16–18}. However, opinions vary as to whether the hydrothermal fluids primarily discharged on mid-ocean ridges creating global Fe^{2+} -rich oceans, or in BIF-forming basins creating local Fe^{2+} -rich brine pools, such as those in the Red Sea¹⁷. The widespread occurrence of massive siderite beds in pre-1.8-Gyr sedimentary sequences suggests that the required conditions for siderite formation were more common and widespread in pre-1.8-Gyr oceans. These conditions were most probably created by a CO_2 -rich atmosphere (see below).

We have carried out petrological, mineralogical and geochemical investigations of massive siderite beds in three major sedimentary sequences, the 1.9-Gyr Gunflint Iron Formation, the 2.6-Gyr Wittenoon Formation and the 2.75-Gyr Helen Iron Formation (Methods and Supplementary Tables). The results of our investigations support the following suggestions made by previous inves-

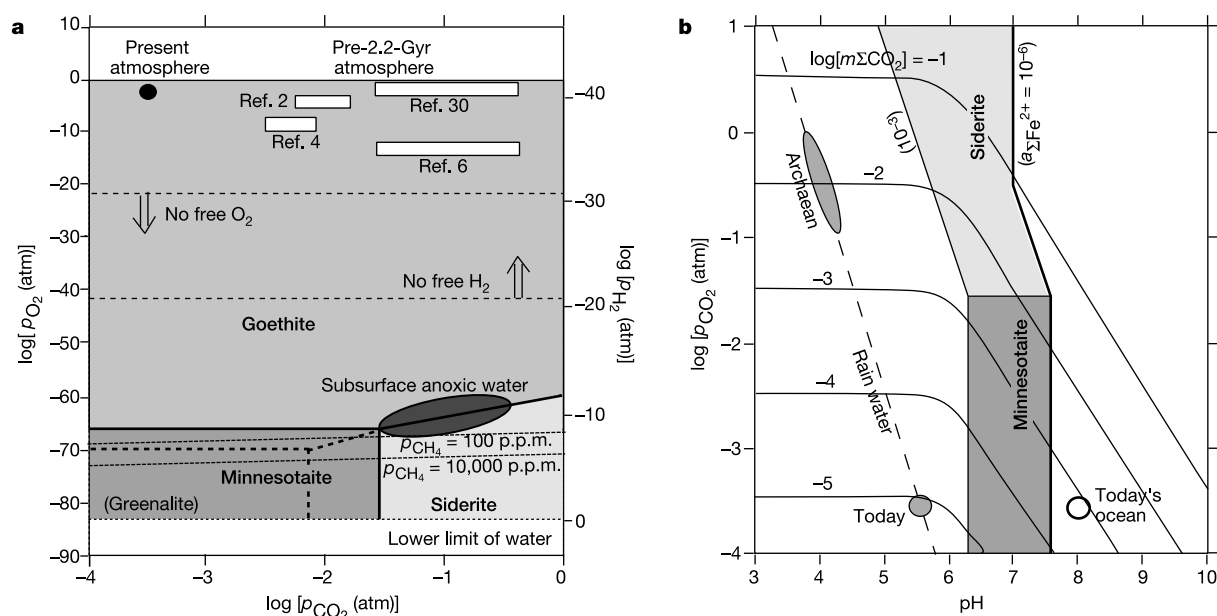


Figure 2 Thermodynamic conditions for the formation of siderite. **a**, A projection of the stability fields of major Fe-bearing minerals on a p_{O_2} (g)– p_{CO_2} (g) plane at $T = 25^\circ\text{C}$ and $\text{SiO}_{2(\text{aq})} = 10^{-3.4}$ moles per kg H_2O (24 p.p.m.); the diagram was constructed using the available thermodynamic data^{28,29}. Note that when $\text{SiO}_{2(\text{aq})} > 10^{-4.35}$ (>2.7 p.p.m.), the stability field of greenalite (shown by dotted lines) disappears but that of minnesotaite appears. The maximum p_{O_2} values for other Fe^{2+} -rich minerals, such as fayalite (olivine) and annite (biotite), fall within ± 5 log units of the minnesotaite–goethite boundary²⁹. Also shown are the p_{O_2} – p_{CO_2} values estimated by previous researchers^{2,4,6,7} for the ~ 2.75 -Gyr atmosphere. Although methane (CH_4) is thermodynamically unstable at $p_{\text{O}_2} \geq 10^{-60}$ atm, a significant amount of CH_4 may survive at higher p_{O_2} conditions, as in today's atmosphere, if the production rate of biogenic CH_4 exceeds the oxidation rate. The shaded area represents the typical conditions for modern subsurface anoxic waters with abundant anaerobic organisms⁸. **b**, A projection of the formational conditions of siderite and minnesotaite on a p_{CO_2} (g)–pH plane when $p_{\text{O}_2} \leq 10^{-60}$ atm,

$\text{SiO}_{2(\text{aq})} = 10^{-3.4}$ m and $\Sigma\text{Fe}^{2+} = 10^{-6}$ – 10^{-3} m. Henry's law constant relates $p_{\text{CO}_2}(\text{g})$ to the concentration of aqueous CO_2 in solution ($m\text{CO}_{2(\text{aq})}$), and the first and second dissociation constants of carbonic acids relate $m\text{CO}_{2(\text{aq})}$ to $m\text{HCO}_3^-$ and $m\text{CO}_3^{2-}$ at a specific pH. $m\Sigma\text{CO}_3^{2-} = m\text{CO}_2(\text{aq}) + m\text{HCO}_3^- + m\text{CO}_3^{2-}$. At $T = 25^\circ\text{C}$, rainwater pH is related to atmospheric p_{CO_2} by: $\text{pH} = 3.91 - 0.5 \log p_{\text{CO}_2}(\text{g})$ (ref. 30), suggesting that the Archean rainwater pH was between ~ 4.4 and ~ 3.9 , if the atmospheric p_{CO_2} was between 0.1 and 1.0 atm. Typical pH values of modern surface waters on land (soil-, ground- and river waters) are ~ 7 and those of ocean waters are ~ 8.1 (ref. 8); the increases from the rainwater pH (5.7) were caused by reactions with various minerals and evaporation. As a first-order approximation, we may expect that the differences in pH values among Archean surface waters were similar to those of modern surface waters, suggesting that the pH values of normal Archean oceans were between ~ 5.5 and ~ 7.5 . This pH range coincides with the formational conditions for siderite.

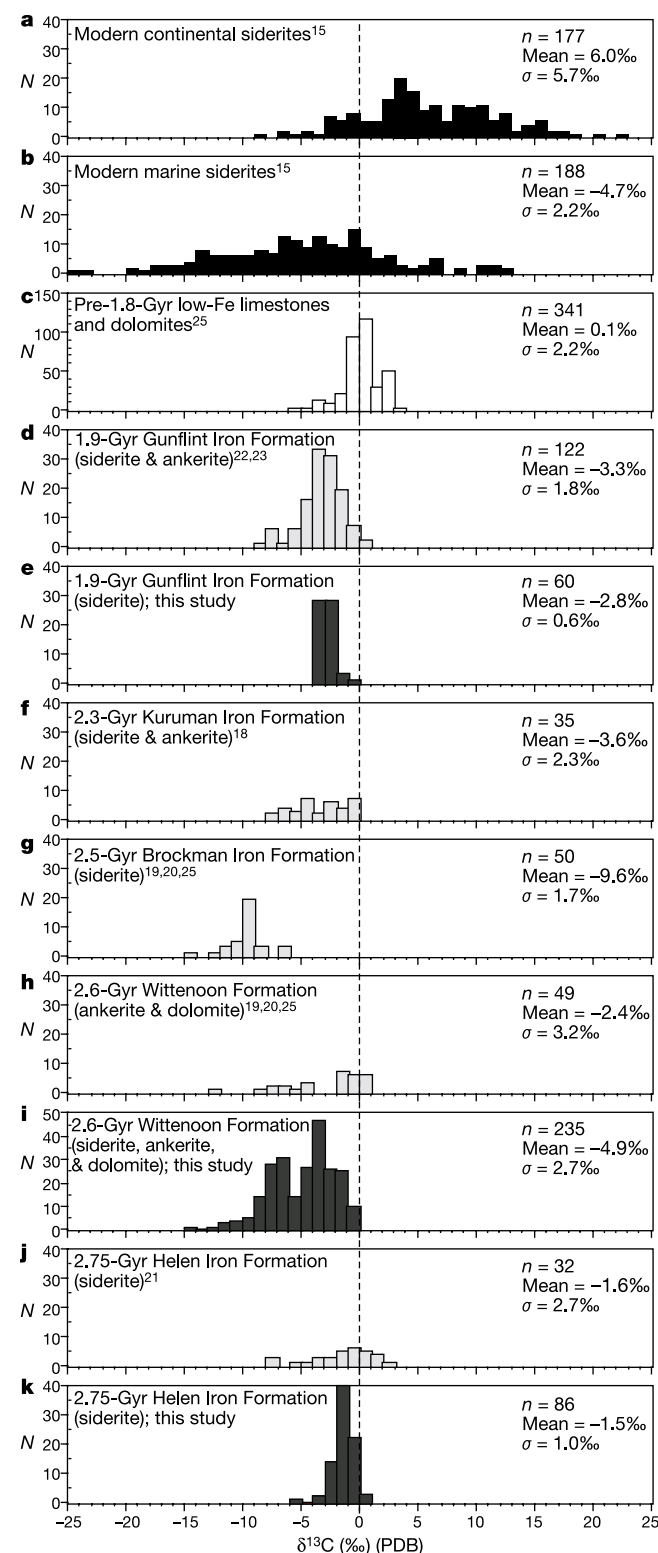


Figure 3 Comparison of the carbon isotopic compositions ($\delta^{13}\text{C}$ values) of carbonates in various rocks. **a, b**, Siderites in modern sediments; **c**, pre-1.8-Gyr Fe-poor (<1 wt% Fe) limestones and dolomites; **d–k**, pre-1.8-Gyr massive siderite-rich sedimentary rocks. We note that the $\delta^{13}\text{C}$ values of pre-1.8-Gyr massive siderite beds are distinctly different from those of modern siderites that formed in terrestrial environments where a significant fraction of the ΣCO_3^{2-} was produced by methanogens. The $\delta^{13}\text{C}$ data on pre-1.8-Gyr massive siderite beds can best be explained if ~70 to ~95% of the ΣCO_3^{2-} used in the siderite formation were derived from normal ocean water and the remaining ΣCO_3^{2-} from the decomposition of marine organic matter by non-methanogenic microbes.

tigators^{18–23}: (1) pre-1.8-Gyr massive siderite-rich beds are mostly composed of Fe-rich carbonates and chert (silica-rich chemical precipitates) with very minor components of detrital minerals (for example, clays, feldspars); (2) siderite is typically the earliest carbonate mineral in these beds, often followed by ankerite, dolomite and calcite; (3) the $\delta^{13}\text{C}$ values of pre-1.8-Gyr Fe-poor carbonates largely fall within a range of $0 \pm 2\text{‰}$ (Fig. 3c), which is also the typical range for normal marine carbonates of younger geologic age^{24,25}; however, those of pre-1.8-Gyr Fe-rich carbonates are generally negative (Fig. 3d–k). From $\delta^{13}\text{C}$ values of around -5‰ for siderites in the Kuruman Iron Formation (Fig. 3f), Beukes *et al.*¹⁸ suggest that hydrothermal fluids provided CO_2 , as well as Fe^{2+} , for the siderites. However, this hydrothermal model does not explain the frequent occurrences of massive siderite beds with more negative $\delta^{13}\text{C}$ values (for example, $< -10\text{‰}$ in the Brockman Iron Formation) or near 0‰ values (for example, the Helen Iron Formation).

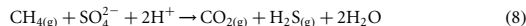
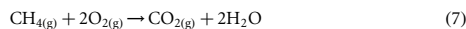
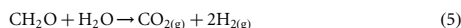
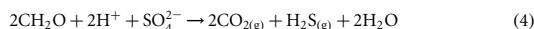
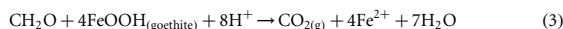
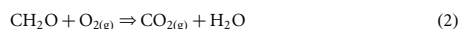
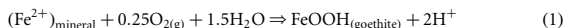
We also agree with the following interpretations made by previous investigators^{19–23} on the above characteristics of pre-1.8-Gyr siderite-rich sedimentary rocks: (1) most siderite crystals directly precipitated from overlying sea water in restricted basins, rather than from pore waters during sediment diagenesis; and (2) the ΣCO_3^{2-} in basin water was a mixture of normal sea water ΣCO_3^{2-} ($\delta^{13}\text{C} = 0 \pm 2\text{‰}$) and biogenic ΣCO_3^{2-} ($\delta^{13}\text{C} = -30 \pm 5\text{‰}$) generated from the decomposition of organic matter ($\delta^{13}\text{C}$ typically between -35 and -20‰) by aerobes and non-methanogenic anaerobes (see reactions (3)–(5) in Methods). The $\delta^{13}\text{C}$ values of pre-1.8-Gyr massive siderite beds (Fig. 3d–k) suggest that the proportion of these two types of ΣCO_3^{2-} varied with time (stratigraphy). These variations were probably due to changes in microbial activity during the history of sedimentary basins; yet the water body in each basin had a characteristic range of $\delta^{13}\text{C}$ values at any given time. Simple isotope mass balance calculations suggest that the percentage of ΣCO_3^{2-} from normal sea water ($\delta^{13}\text{C} \approx 0\text{‰}$) in the mixtures varied from ~70% for the Brockman Iron Formation to ~95% for the Helen Iron Formation (Fig. 3d–k). Findings of organic matter with very low $\delta^{13}\text{C}$ values ($\sim -50\text{‰}$) in some ~2.7-Gyr sedimentary rocks in the Hamersley Basin led Hayes²⁶ to suggest a basin environment where methanogens and methane oxidizers (methanotrophs and/or sulphate reducers) were actively producing biogenic $\text{CO}_{2(\text{aq})}$ with $\delta^{13}\text{C} \ll -30\text{‰}$ (see reactions (6) and (7) in Methods). If such CO_2 was involved in the formation of siderites in the Brockman Iron Formation, the percentage of normal sea water ΣCO_3^{2-} would have been $\geq 70\%$.

The above discussion leads us to conclude that the ΣCO_3^{2-} source for pre-1.8-Gyr siderites was principally contemporaneous sea water. Widespread, thick siderite-rich beds before ~1.8 Gyr ago occur because the ΣCO_3^{2-} concentration of normal oceans was $\geq 10^{-2.5} \text{m}$ and the pH was between ~5.5 and ~7.5; these were consequences of an atmospheric $p_{\text{CO}_2} > 10^{-1.4 \pm 0.2} \text{atm}$ and a rainwater pH < 4.4 (Fig. 2b). This minimum p_{CO_2} value is more than an order of magnitude higher than the p_{CO_2} values of Pavlov *et al.*^{4,5,27} (for example, $10^{-2.6} \text{atm}$ at 2.75 Gyr ago), further implying that the atmospheric p_{CH_4} was much lower than the values they estimated (Fig. 1). Our minimum p_{CO_2} value is compatible with the p_{CO_2} range estimated by Kasting⁶ (for example, $10^{-1.2}$ to $10^{+0.2} \text{atm}$ at 2.75 Gyr ago; $10^{-1.8}$ to $10^{-0.7} \text{atm}$ at 2.0 Gyr ago; Fig. 1), based on the assumption that CO_2 was the only major greenhouse gas. However, in order to increase the accuracy in estimating atmospheric p_{CO_2} values during the Archaean and Proterozoic eras, we must obtain accurate information on the global climate change, as well as the chemical and isotopic characteristics of Fe-rich carbonates of various age. Our study highlights the need to investigate the impacts of higher atmospheric p_{CO_2} , higher oceanic ΣCO_3^{2-} , lower rainwater pH and lower oceanic pH on global geochemical cycles and on the biota in the oceans and on land. □

Methods

Controls on p_{O_2} and p_{CO_2} values of subsurface waters

The following reactions involving Fe-bearing minerals and organic matter (CH_2O) play important roles in controlling the p_{O_2} and p_{CO_2} of subsurface waters:



Reactions (1) and (2) are typically carried out by aerobic organisms while reactions (3)–(6) are carried out by anaerobes: reaction (3) by Fe^{3+} reducers, reaction (4) by sulphate reducers, reaction (5) by fermenters and reaction (6) by methanogens. The oxidation of CH_4 to CO_2 may be carried out by methanotrophs in reaction (7) and/or sulphate reducers in reaction (8).

According to Henry's law constant for O_2 (ref. 28) and Avogadro's number, the concentration of dissolved O_2 ($mO_{2(aq)}$) in water is $10^{-2.90}$ moles per kg H_2O ($= 10^{20.88}$ molecules per kg H_2O) when the water is in equilibrium with an atmosphere at $p_{O_2(g)} = 1$ atm and $T = 25^\circ C$. Free O_2 molecules disappear from a kilogram of water at $mO_{2(aq)} = 10^{-23.78}$ (that is $p_{O_2(g)} \approx 10^{-21}$ atm) (Fig. 2a). Below this value, the $mO_{2(aq)}$ (and $p_{O_2(g)}$) are 'virtual values' that are 'calculated' from the number of $H_{2(aq)}$ molecules by assuming equilibrium in the reaction: $H_{2(aq)} + 1/2O_{2(aq)} = H_2O$. Therefore, reactions (1) and/or (2) alone may reduce the p_{O_2} of subsurface waters to $\sim 10^{-21}$ atm, but H_2 generation by reaction (5) is required to decrease the p_{O_2} to $\leq 10^{-60}$ atm where Fe^{2+} -rich silicates (for example, minnesotaite) and/or siderite may form. Microbial decomposition of organic matter (reactions (2)–(6)) may also create the other conditions necessary for siderite formation in modern sediments: increases in p_{CO_2} from $\sim 10^{-3.5}$ to $>10^{-1.4}$ atm and in ΣCO_3^{2-} from $\sim 10^{-3.2}$ to $>10^{-2.5}$ m. The increased p_{CO_2} may then decrease pH from 8.1 to <7.5 , mainly through the reaction $CO_{2(g)} + H_2O = H^+ + HCO_3^-$. Organic acids, generated from organic matter decomposition, also contribute to lowering the pH and also play an important role in leaching iron from rocks²⁸ to increase the concentration of ΣFe^{2+} in pore waters from $\ll 10^{-6}$ to $>10^{-6}$ m (reaction 3).

Mineralogical and geochemical investigations of siderite-rich rocks

To confirm some of the major suggestions made by previous investigators^{18–23} on the origins of pre-1.8-Gyr massive siderite beds, we have carried out our own investigations, focusing on microscale variability in mineralogical, chemical and isotopic characteristics of three major siderite-rich sedimentary formations. We selected four specimens of the 2.7-Gyr Helen Iron Formation in the Michipicoten district, Ontario, Canada, 45 specimens of the 2.6-Gyr Wittenoon Formation in the Hamersley district, Western Australia and three specimens of 1.9-Gyr Gunflint Formation in the Thunder Bay district, Ontario, Canada.

We have examined the textural relationships of various carbonates in thin sections from these samples using petrographical and electron microscopes. From each of the specimens, 1 to 30 powdered samples were microdrilled, and a total of 381 powdered samples were analysed for: (1) the abundance ratios of minerals (siderite, ankerite, dolomite, calcite, quartz and so on) using an X-ray diffractometer; (2) the abundance ratios of Fe, Mn, Mg and Ca using an atomic absorption spectrometer; and (3) the $\delta^{13}C$ and $\delta^{18}O$ values using a Finnigan 242 mass spectrometer. The contents and $\delta^{13}C$ values of kerogen in the powdered samples were also determined using a Carlo Erba elemental analyser and the mass spectrometer, respectively. The chemical and isotopic data are presented in the Supplementary Information.

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Low electrical resistivity associated with plunging of the Nazca flat slab beneath Argentina

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Beneath much of the Andes, oceanic lithosphere descends eastward into the mantle at an angle of about 30° (ref. 1). A partially molten region is thought to form in a wedge between this descending slab and the overlying continental lithosphere as volatiles given off by the slab lower the melting temperature of