could be an important factor in their association with some neurodegenerative diseases (15) and might allow their dissociation into oligomers, which can interact with cellular components. The differences between the moduli of mature amyloid fibrils and HbS fibrils further highlight the different balance of inter- versus intramolecular interactions. Thus, in both cases, a sizeable fraction of residues participates in hydrogen bonds: within α helices for HbS and within β sheets for amyloid fibrils. However, for HbS fibrils, these bonds are all within one individual molecule, and the intramolecular interactions are mediated by weaker surface interactions; on the other hand, for amyloid fibrils, some or all of the hydrogen bonds are intermolecular when they can contribute to the long-range stability of the fibril and the high elastic modulus. These conclusions are exemplified by the orb-weaving spider’s use of two forms of silk. Dragline silk, which contains a high fraction of densely hydrogen-bonded domains, is used to provide the structural scaffold for the web (27) and has an elastic modulus that is comparable to hydrogen-bonded cross-β protein nanofibrils (Fig. 2). On the other hand, web capture silk, which serves for arresting prey, is a viscid biofilm containing cross-linked polymer networks and has an elastic modulus that is comparable to that of elastomers such as rubber and elastin (27).

The finding that the rigidity of amyloid fibrils is described by a common elastic modulus, defined predominantly by intramolecular interactions involving the common polypeptide main chain, provides quantitative evidence for the idea (2) that these structures form a generic class of material. In addition, our results provide insight into the changes in the distribution of inter- versus intramolecular bonding interactions associated with the transition of proteins from their native globular structures into polymeric supramolecular assemblies. Finally, comparisons between artificial self-assembling protein fibrils and natural cellular structures exemplify the design criteria used in nature to select materials for structural applications and provide inspiration for the design of novel nanoscale biomaterials.

References and Notes

11. Materials and methods are available as supporting material on Science Online.
30. Single-letter abbreviations for the amino acid residues are as follows: A, Ala; C, Cys; D, Asp; E, Glu; F, Phe; G, Gly; H, His; I, Ile; K, Lys; L, Leu; M, Met; N, Asn; P, Pro; Q, Gln; R, Arg; S, Ser; T, Thr; V, Val; W, Trp; and Y, Tyr.
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Supporting Online Material

www.sciencemag.org/cgi/content/full/318/5858/1900/DC1
Materials and Methods
Figs. S1 and S2
References
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A Sulfur Dioxide Climate Feedback on Early Mars

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Ancient Mars had liquid water on its surface and a CO2-rich atmosphere. Despite the implication that massive carbonate deposits should have formed, these have not been detected. On the basis of fundamental chemical and physical principles, we propose that climatic conditions enabling the existence of liquid water were maintained by appreciable atmospheric concentrations of volcanically degassed SO2 and H2S. The geochemistry resulting from equilibration of this atmosphere with the hydrological cycle is shown to inhibit the formation of carbonates. We propose an early martian climate feedback involving SO2, much like that maintained by CO2 on Earth.

Martian geomorphology indicates the existence of liquid surface water, perhaps even an ocean (1), during the late Noachian epoch [~3.8 × 109 years ago (2)], when surface temperatures were marginally above freezing (3) but still considerably warmer than at present. The element conditions are most likely explained by an optically thicker atmospheric greenhouse (4) that may also have had to compensate for a dimmer sun (5). A CO2-rich atmosphere could have been supplied by vigorous volcanism associated with the emplacement of the Tharsis igneous province (6) as well as with earlier episodes of crustal formation. Although attempts at explaining the existence of liquid water with an atmosphere of pure CO2 are complicated by CO2 condensation (7), the possible existence of infrared-reflective CO2 ice clouds (8) or atmospheric heating due to absorption of solar radiation by trace amounts of SO2 (9) has been suggested to resolve this difficulty.

If early volcanic activity on Mars did sustain a thick CO2 atmosphere, one might expect the existence of a carbon cycle similar to Earth’s, where the release of CO2 from volcanoes is balanced by burial of calcium carbonate through silicate weathering reactions that remove protons and release alkalinity to seawater (10). The dependence of silicate weathering on temperature and precipitation creates a negative feedback on the atmospheric abundance of CO2, stabilizing the climate to maintain surface conditions with adequate liquid water for weathering as long as the volcanic release of CO2 continues. Existence of such a carbon cycle on Mars would have left carbonate sediments at the surface as well as abundant clays left over from the weathering process. For example, a carbon outgassing flux of 7 × 103 mol C year−1, about the same as the modern volcanic outgassing rate on Earth (11), maintained for 108 years would result in a global carbonate layer ~180 m thick. The same mass of carbonate precipitated in an ocean covering 30% of Mars (1) would form a layer ~600 m thick.

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The virtual absence of carbonate minerals above the detection limit of a few weight percent (12), coincident with evidence for an early climate warm enough for liquid water, is therefore puzzling.

A possible resolution of this contradiction may involve the abundance of sulfur on the surface of Mars. Martian soil and rock analyses show significant enrichment in sulfur relative to terrestrial soils (13); recent analysis of data obtained by the rovers identified soils with sulfur contents as high as 7.5 weight % SO₃ (14). Like carbon, sulfur in some forms can play an important role in radiative forcing and in silicate weathering. In this paper, we explore the implications of an active sulfur cycle, linked to the carbon cycle, on the climate and surface chemistry of early Mars.

In an early martian sulfur cycle, volcanic outgassing of sulfur to the atmosphere and surface environment, primarily as SO₂ and H₂S, would be balanced by photochemical sinks and precipitation of sulfur-bearing minerals. The modern martian atmosphere is relatively oxidized after billions of years of hydrogen escape (15), although earlier in martian history oxygen escape (16) as well as emission of reduced gases from hydrothermal alteration of basaltic crust (17) likely resulted in a more reducing atmosphere. During the emplacement of Tharsis as with any period of high, sustained volcanism, the additional emission of reduced gases, including H₂S and SO₂, would drive the oxidation state even lower. The lifetime of sulfur species that today are rapidly oxidized in Earth’s atmosphere is longer under such conditions. In the absence of biological catalysis, kinetic barriers to changes in the valence state of sulfur would enable the coexistence of atmospheric and aquatic sulfide (S²⁻), sulfite (S⁴⁺), and carbonate (CO₃²⁻) in proportions depending on the relative magnitudes of their sources and sinks.

In an atmosphere with significant quantities of reduced sulfur gases, SO₂ would play a particularly important role, not only climatically as a powerful greenhouse gas but also in the chemistry of the surface environment. SO₃ is highly soluble in water, so its early martian geochemical cycle would have been dominated by aquatic reservoirs, such as a northern hemisphere ocean (1) or regions of sustained groundwater upwelling (18). The presence of even a small amount of SO₂ in a CO₂-rich atmosphere lowers the pH of surface waters, suppressing carbonate precipitation in favor of sulfite minerals. The resulting geochemical cycle is analogous to the terrestrial carbon cycle (10), with a silicate weathering feedback on climate involving SO₂ instead of CO₂ and the pH of water bodies buffered by the solubility of sulfite minerals and the partial pressure of SO₂ instead of the solubility of calcite and the partial pressure of CO₂.

Details of this geochemical cycle depend on relative rates of sulfur outgassing, photochemical transformations, silicate weathering, and mineral precipitation. Sulfur outgassing from Tharsis is limited by the solubility of sulfur in basaltic melts. The sulfur content of martian melts has recently been estimated at 1400 parts per million (ppm) (19), one to three times the concentration in Hawaiian lavas (20). Degassing of the entire volume of Tharsis magma [3 × 10⁶ km³ (6)] implies a maximum flux of ~4 × 10¹⁶ mole S year⁻¹ if the emplacement of Tharsis took 10⁸ years. This is about twice the present sulfur outgassing flux on Earth [~13 × 10⁶ metric tons SO₂ year⁻¹ (21)], although its impact on the surface of Mars would have been much greater given the smaller volume of the atmosphere. Because the speciation of sulfur coming from volcanic outgassing depends on the oxygen fugacity of the magmat, the oxidation state of martian basalts (22) implies that at least 50% of the sulfur, or ~2 × 10¹¹ mole S year⁻¹, was emitted as H₂S (23).

Removal of SO₂ from the atmosphere normally occurs by gas-phase oxidation, by reaction pathways after photolysis, and by a variety of physical sinks leading to deposition and subsequent oxidation. The reducing power from volcanic fluxes of H₂S and SO₂ described above, combined with hydrothermal emission of hydrogen and methane, would compensate for even the most optimistic estimates of hydrogen escape [summarized in (16)], implying decreased gas-phase oxidation of SO₂ (24). Furthermore, deposition of SO₂, typically followed by rapid heterogeneous oxidation, would instead lead to saturation of the martian surface and return fluxes to the atmosphere at steady state (25). Aqueous disproportionation of sulfite could potentially prevent saturation of the aquatic reservoir with species of S⁴⁺ (26). However, the rates of these reactions in the absence of biological catalysis have only been examined above 10⁶°C (27) and are likely slow at low temperature [Supporting Online Material (SOM) text].

It has been suggested that reaction of the products of SO₂ photolysis with atmospheric oxidants recycles SO₂, resulting in little net loss (28). However, a low abundance of oxidants limits these reactions as well, introducing another potentially important sink: SO₂ photolysis followed by disproportionation to sulfate and elemental sulfur (29). This sink was likely of low magnitude under early martian conditions, because a higher ultraviolet flux attributed to the young Sun (30) would have occurred in wavelengths where absorption and Rayleigh scattering by a thick CO₂ atmosphere afforded significant shielding (31). Moreover, the absorption of sulfur volatiles, including S₈ possibly generated by SO₂ photochemistry (25), would have further attenuated the energy available for SO₂ photodissociation (fig. S1). Wong et al. (32) simulated the local atmospheric chemical impact of a volcanic event on the present oxidizing martian atmosphere, calculating a mixing ratio of more than 100 ppm SO₂ in the lower 60 km of the atmosphere and a very low photolysis rate constant of 6.1 × 10⁻¹⁸ s⁻¹ at an altitude of 10 km. During the emplacement of Tharsis, a volcanic flux several orders of magnitude higher, sustained over hundreds of millions of years, means that the photolysis sink was unlikely to be of primary importance.

Accumulation of 10⁻⁶ to 10⁻⁷ bars of SO₂ in a CO₂-rich atmosphere, made possible by its small total photochemical sink and by saturation of the surface, would have had a substantial radiative effect (33), perhaps enough to have maintained liquid water on the surface of early Mars. Under such conditions, temperature and precipitation are much more sensitive to changes in the partial pressure of SO₂ (pSO₂) than to changes in the...
partial pressure of CO₂ (pCO₂), mainly because of the large difference between the atmospheric abundances of SO₂ and CO₂ but also because of saturation of the infrared absorption lines of CO₂. Additionally, because of the high solubility of SO₂, most of the S⁴⁺ would have been present in the aquatic reservoir and would have had a dominant role in the surface environment. Because hydration of SO₂ forms sulfurous acid (H₂SO₃), which is much stronger than carboxylic acid (34), the pH of water in equilibrium with CO₂ and SO₂ is essentially independent of concentrations. Thin dashed lines mark the critical value of pSO₂/pCO₂ above which concentrations are limited by saturation of sulfite rather than carbonate minerals. 

**Fig. 2.** Cation concentration limits imposed by sulfite (black) or carbonate (gray) mineral saturation as a function of pSO₂/pCO₂. Top) CA mineral saturation and (bottom) Mg mineral saturation. The curves are solid in the range of pSO₂/pCO₂ in which precipitation of the represented mineral is the limiting factor on cation concentrations. Thin dashed lines mark the critical value of pSO₂/pCO₂ above which concentrations are limited by saturation of sulfite rather than carbonate minerals.

**Fig. 3.** Time (t) evolution of pSO₂, pCO₂ (top), surface water pH (middle), and the precipitated mineral assemblage (bottom), for (A) 70% and (B) 20% photochemical destruction of all SO₂ outgassed or produced. The volcanic outgassing rate during this simulation was 2 × 10¹¹ mole year⁻¹ SO₂ and H₂S, each. Note that the onset of calcium sulfite and ferrous carbonate precipitation (vertical dashed lines) is accompanied by a decrease in pH because of removal of alkalinity and an increase in pCO₂ because of water body acidification.

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balance SO₂ outgassing would be relatively low, perhaps just above the temperature necessary to sustain liquid water. This result is consistent with geochemical evidence that Mars in the late Noachian was likely never very warm (3).

To explore this feedback cycle, we constructed a model of the sulfur and carbon cycles of early Mars, including an ocean covering ~30% of the planet, an area about equivalent to the area covered by the Vastitas Borealis Formation, inferred from Martian meteorites (1). The model tracks the evolution of the surface (-42) reservoirs of carbon, the sulfur in its different valence states, and the dissolved reservoirs of weathering-derived cations and SiO₂. Carbon is supplied by volcanic emission of CO₂ and removed by carbonate mineral precipitation. SO₂ (S4+) and H₂S (S2-) are last to precipitate, leaving the aquatic reservoir and despite water body acidification, the existence of liquid surface water. The SO₂ climate feedback described above stabilized surface temperature, with precipitation of sulfite minerals from mildly acidic surface solutions preventing massive carbonate precipitation while allowing the formation of clays.

When volcanism subsided, SO₂ was rapidly removed from the atmosphere by continued photolysis and by reaction with oxidants, now supplied at a faster rate than reduced gases. Without the radiative contribution of SO₂, the surface temperature dropped below the freezing point of water, surface water bodies froze, becoming more concentrated and precipitating the remaining ions in a progression of increasingly soluble salts. Water frozen at the surface was gradually redistributed by sublimation and refreezing because of seasonal cycling and changes in obliquity (44).

Under a now-oxidizing atmosphere, sulfite minerals at the surface would be episodically exposed to small amounts of surface or ground water and altered to sulfate, releasing acidity that would be stored in the soil. This oxidation of sulfites, in combination with oxidation of siderite and pyrite, is one possible way of creating the acidic environment proposed for later periods in martian history (45, 46) as well as the observed surface mineralogy. If the high volcanic flux persisted for 10⁶ years accompanied by precipitation of sulfite minerals, elemental sulfur, and perhaps sulfides, then the supply of oxidants associated with hydrogen escape (16) would require a billion years to transform all of the precipitates to sulfate. A shorter duration of element conditions would imply a shorter oxidation time scale.

Despite subfreezing surface temperatures, the early geothermal gradient of Mars was high enough to maintain hydrothermal circulation in the crust (47). Subsurface silicate weathering coupled with carbonate mineral precipitation in crustal pores and fractures would have slowly removed the remaining atmospheric CO₂, consistent with the carbonate minerals found in veins in some martian meteorites (48). Estimates of martian crustal porosity (49) easily accommodate several bars of CO₂ sequestered in carbonate minerals. Three billion years of this process, in combination with atmospheric loss associated with large impacts and more efficient molecular escape after termination of the magnetic field of Mars, resulted in the present thin CO₂ atmosphere. Our hypothesis for a SO₂ climate feedback successfully accounts for salient features observed on the surface of Mars and in the martian meteorites (13, 14, 41, 48, 50). Validation of our hypothesis would come from detection of sulfites on the martian surface, although the exclusion of sulfites from spectral libraries used for mineral detection on Mars, along with their tendency to oxidize, might make such detection difficult. Our hypothesis should apply to any planet with a reducing atmosphere and volcanically outgassed SO₂ and may also explain the apparent scarcity of carbonate sediments in the Archean Earth (51).

References and Notes
Coupled $^{142}$Nd-$^{143}$Nd Isotopic Evidence for Hadean Mantle Dynamics

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The oldest rocks—3.85 billion years old—from southwest Greenland have coupled neodymium-142 excesses (from decay of now-extinct samarium-146; half-life, 103 million years) and neodymium-143 excesses (from decay of samarium-147; half-life, 106 billion years), relative to chondritic meteorites, that directly date the formation of chemically distinct silicate reservoirs in the first 30 million to 75 million years of Earth history. The differences in $^{142}$Nd signatures of coeval rocks from the two most extensive crustal relics more than 3.6 billion years old, in Western Australia and southwest Greenland, reveal early-formed large-scale chemical heterogeneities in Earth’s mantle that persisted for at least the first billion years of Earth history. Temporal variations in $^{142}$Nd signatures track the subsequent incomplete remixing of very-early-formed mantle chemical domains.

Isotope data for short-lived decay schemes such as the $^{146}$Sm-$^{142}$Nd system [half-life ($T_{1/2}$), 103 million years (My)] obtained from samples of the Moon, Mars, and meteorites are revealing the complexities of early planetary differentiation that occurred soon after accretion [e.g., (1–4)]. Attempts to demonstrate $^{142}$Nd variations in Earth were initiated in the 1990s (5), with recent measurements of some ancient rocks [dating from >3.6 billion years ago (Ga)] (6–10) now firmly establishing variable $^{142}$Nd/$^{144}$Nd ratios in Earth relative to modern terrestrial compositions. This is important because detectable $^{142}$Nd isotopic variations can only be generated from Sm/Nd fractionation during the largely unknown first ~300 My of Earth history, while $^{146}$Sm is still actively decaying. Previous studies focused largely on the ~3.7- to ~3.8-billion-year (Gy)-old regions of the Isua supracrustal belt of West Greenland, representing largely one, albeit important, spatial and temporal point in Earth evolution. Interpreting the large range of reported $^{142}$Nd/$^{144}$Nd ratios [0 to 17 parts per million (ppm)] higher than modern terrestrial compositions in terms of early planetary processes is complicated because many of the analyzed rocks were either metasedimentary mixtures of eroded terranes (7–9) or metabasalts (6, 9, 10) from areas that experienced widespread secondary chemical alteration (e.g., [11, 12]).

Tantalizing hints of Hadean Era (~4.0 Ga) Earth dynamics come from the recent recognition that all crust and upper mantle rocks today have a $^{142}$Nd/$^{144}$Nd excess of ~20 ppm compared with primitive chondritic meteorites (2, 13, 14), which were the building blocks of Earth. This requires not only that chemically distinct domains with high and low Sm/Nd, evolving to high and low $^{142}$Nd, respectively, formed during or soon after accretion but also that these domains must have persisted in the present to account for the continued isotopic offset between chondrites and modern terrestrial rocks. Additionally, the more extreme $^{142}$Nd excesses measured in some Archean rocks (6, 7, 9, 10) require the early existence of an older, or more severely depleted (higher Sm/Nd) mantle, whose extent and longevity is unknown. To track the origin, distribution, and interaction of these global chemical domains requires precise $^{142}$Nd data for ancient rocks with a range of ages and from a variety of localities.

Here, we present high-precision $^{142}$Nd data (Table 1) (15) combined with $^{142}$Nd data from samples of the two most aerially extensive >3.6-Gy-old terranes: the 3000 km² Isua Complex (16) of southern West Greenland, of which the Isua supracrustal belt is one component, and the Narryg Gneiss Complex of the Yilgarn craton, Western Australia. In contrast to previous studies, the emphasis is on analysis of the oldest tonalites, a juvenile granite rock type typically representing the earliest formed continental crust in a region and from which direct age information in the form of U-Pb zircon ages can be obtained. Archean tonalites are melts of young oceanic crust [e.g., (17)], derived from the upper mantle. The intermediate basalt stage is likely short compared with the time scale of $^{147}$Sm decay and with Sm/Nd similar to that of the mantle source.

The Isua samples span a 210-My age range (3.64 to 3.85 Gy old) and include crystalline rocks from newly recognized localities of homogeneous 3.85-Gy-old tonalites (18) and >3.85-Gy-old mafic rocks (15). These samples are some of the oldest terrestrial rocks yet discovered. The two 3.73-Gy-old Narryg Gneiss Complex tonalitic gneisses are the oldest rocks from the Australian continent (19). All rocks are from our field collections and represent the most geologically pristine materials, with well-defined crystallization ages having minimal secondary chemical alteration (table S1) (15).

Homogenized powdered samples weighing from 0.1 to 0.3 g were dissolved and processed to isolate >500 ng Nd. The $^{142}$Nd/$^{144}$Nd isotopic compositions were measured as Nd²⁺ on a Triton thermal ionization mass spectrometer using a multidyndamic data collection scheme (9). Measurements of a standard Nd solution run interspersed with the samples yielded an external reproducibility (2 SD) of ±3.5 ppm (fig. S1) (in-run precisions were from 1.0 to 2.5 ppm, 2 SE). Replicate analyses of 14 modern rocks yielded the same external precision as the standard data (fig. S2), which demonstrates the validity of this precision for chemically processed samples. The $^{146}$Sm/$^{144}$Nd data were obtained on separate powder samples using standard isotope-dilution methods (15).

Fifteen samples from the Isua Complex all have well-resolved $^{142}$Nd excesses of 9 to 20 ppm relative to the modern terrestrial reference composition (Table 1). The six basalts with ages

4. The first and second acid dissociation constants of sulfuric acid are $10^{-1.8}$ and $10^{-1.8}$, respectively, whereas those of carbonic acid are $10^{-3.2}$ and $10^{-4.3}$.

5. Pre-industrial atmospheric $p$SO$_2$/pCO$_2$ is $3 \times 10^{-7}$.