

Large sulfur isotope fractionations in Martian sediments at Gale crater

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Variability in the sulfur isotopic composition in sediments can reflect atmospheric, geologic and biological processes. Evidence for ancient fluvio-lacustrine environments at Gale crater on Mars and a lack of efficient crustal recycling mechanisms on the planet suggests a surface environment that was once warm enough to allow the presence of liquid water, at least for discrete periods of time, and implies a greenhouse effect that may have been influenced by sulfur-bearing volcanic gases. Here we report *in situ* analyses of the sulfur isotopic compositions of SO₂ volatilized from ten sediment samples acquired by NASA's Curiosity rover along a 13 km traverse of Gale crater. We find large variations in sulfur isotopic composition that exceed those measured for Martian meteorites and show both depletion and enrichment in ³⁴S. Measured values of δ³⁴S range from -47 ± 14‰ to 28 ± 7‰, similar to the range typical of terrestrial environments. Although limited geochronological constraints on the stratigraphy traversed by Curiosity are available, we propose that the observed sulfur isotopic signatures at Gale crater can be explained by equilibrium fractionation between sulfate and sulfide in an impact-driven hydrothermal system and atmospheric processing of sulfur-bearing gases during transient warm periods.

Sedimentary strata on Mars preserve intriguing evidence for past shifts in climate and environmental conditions, including the fluvio-lacustrine system at Gale crater explored by the Mars Science Laboratory's Curiosity rover¹. In addition, impacts such as the one that formed Gale crater would have imparted a significant amount of thermal energy, affecting regional hydrology and sulfur chemistry for periods lasting several hundred thousand years²⁻⁴. Both atmospheric and geologic processes may have produced isotopic variability in sulfur-bearing minerals that is visible today.

Sulfur isotopic signatures are also interesting in astrobiological context, as depletion in heavy isotopes is characteristic of microbial sulfur metabolisms. Due to uncertainty regarding the stability and ultimate fate of organic compounds under the oxidizing and ionizing surface conditions on Mars⁵, the potential of sulfur isotopes to record biosignatures is a key motivation for their measurement by Curiosity.

Sample acquisition and analytical results

From February 2013 to June 2016, Curiosity travelled ~13 km through sedimentary terrain within Gale crater, climbing ~100 m

in elevation. Ten samples acquired by the rover's drill were processed by the Sample Analysis at Mars (SAM) suite, which employs pyrolysis to release volatile compounds from solid materials for analysis. Geologic context for these samples is summarized in the Supplementary Information and depicted in the stratigraphic column of Fig. 1, which also provides sample identities. Here we report highly variable sulfur isotopic compositions measured during the traverse and discuss implications for the ancient environment of Gale crater.

The evolved gas analysis (EGA) protocol used for SAM experiments and analytical procedures are described in the Supplementary Information. Sulfur isotope ratios (δ³⁴S) for these samples are reported in Supplementary Table 1 and plotted in stratigraphic context in Fig. 1, while SO₂ release profiles are shown in Supplementary Fig. 1. For experiments in which the EGA profile suggests the possibility of more than one sulfur-bearing phase, compositions of multiple phases are reported if possible.

Values of δ³⁴S computed for these samples range from -47 ± 14‰ to 28 ± 7‰ (1σ), representing statistically significant variability even with consideration of 2σ uncertainties. Notably, SO₂ peaks of the Cumberland (CB) and Oudam (OU) samples reveal

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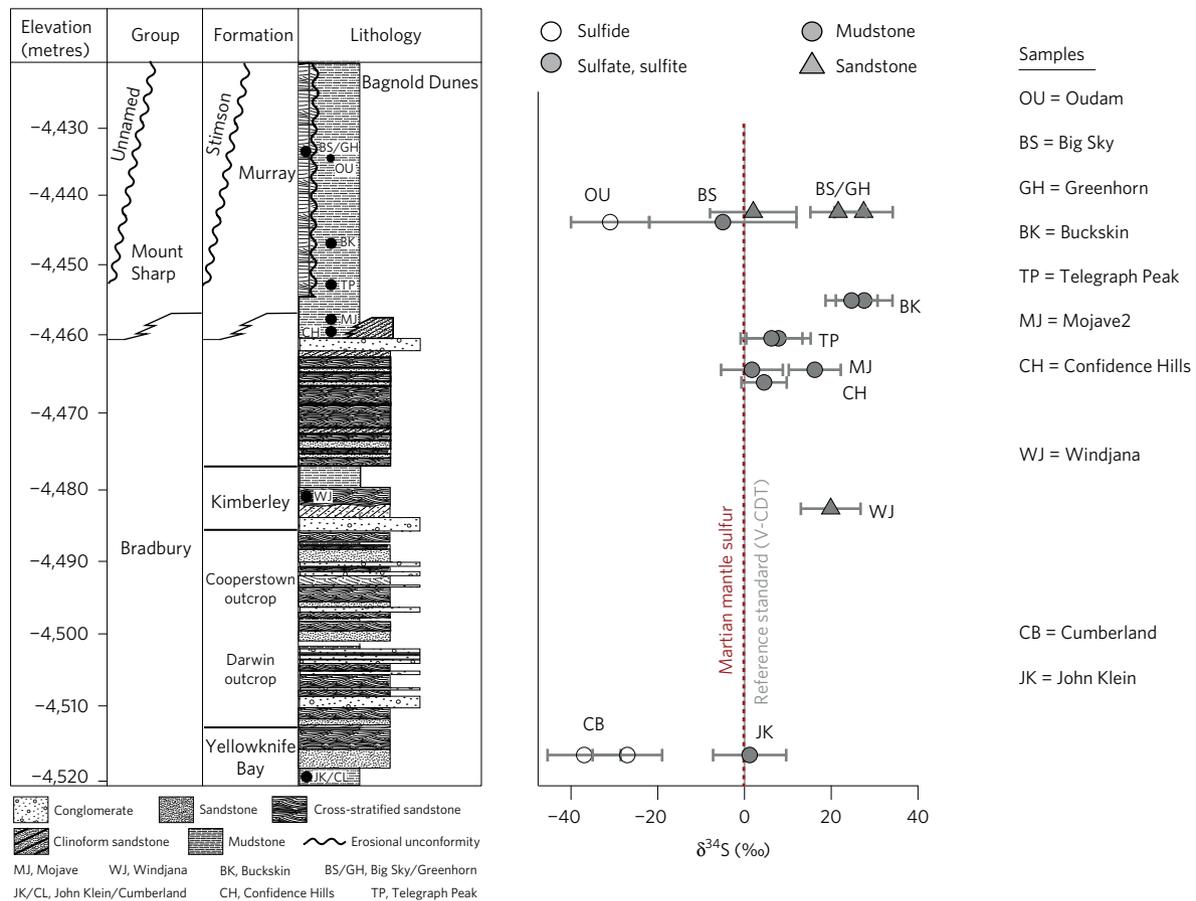


Figure 1 | Measured sulfur isotopic compositions for discrete SO_2 peaks displayed in stratigraphic context. Error bars reflect 1σ uncertainties. Data plotted for the CB sample represent the weighted average of three sample aliquots. Stratigraphic column updated from ref. 1; Martian mantle composition from ref. 6.

significantly ^{34}S -depleted isotopic compositions, while all other samples are close to Vienna Cañon Diablo Troilite (V-CDT) (and Martian mantle sulfur⁶) or enriched in ^{34}S . These new data reveal a much wider range of isotopic fractionation than seen in sulfur-bearing phases of Martian meteorites^{6–12}. The igneous lithologies of meteorites have yielded an estimate of the juvenile Martian sulfur composition⁶ and glimpses of atmospherically processed sulfur incorporated into magmas or as secondary sulfates^{6–12}. However, the lack of an efficient sulfur crustal recycling mechanism on Mars may have facilitated preservation of large isotopic heterogeneities at the planet's surface, reflecting effects of multiple processes occurring at different times. Curiosity's analyses of sedimentary sulfur broaden our perspective on the Martian sulfur cycle by providing direct evidence of reduction–oxidation processes in an environment not previously accessible for exploration.

Sulfur observed at CB and OU, interpreted to derive from sedimentary sulfides, is depleted in ^{34}S by ~ 30 – 40% compared with Martian igneous sulfides⁶ and by 60 – 80% compared with the most enriched compositions observed in samples of the Murray and Stimson formations. Neither igneous processes nor oxidative weathering of igneous sulfides would cause appreciable fractionation of sulfur isotopes. However, both isotope exchange between oxidized and reduced forms of sulfur and atmospheric processes can generate large fractionations, as can kinetic processes associated with reduction and disproportionation of high- and mid-valence sulfur compounds¹³.

Observations by other Curiosity instruments constrain diagenesis of the Sheepbed mudstone to ~ 60 – 80°C (ref. 14) with fluids of circumneutral pH (refs 14,15). Supplementary Fig. 2 shows

the equilibrium sulfur isotopic fractionation expected between aqueous sulfate/sulfide, sulfite/sulfide and total bisulfite/sulfide based on theoretical calculations¹⁶ and indicates approximate times required to reach 90% sulfate/sulfide equilibrium at conditions relevant to Gale crater fluids¹⁷. Although the figure indicates that it is possible to achieve the full range of $\delta^{34}\text{S}$ observed through equilibrium sulfate/sulfide fractionation at 60 – 80°C , kinetic inhibition of this abiotic process at low temperatures argues against its operation within the lakebed sediments as a viable explanation.

Biological fractionation is a potential candidate to explain highly depleted $\delta^{34}\text{S}$ values by analogy to terrestrial processes. The range of $\delta^{34}\text{S}$ (-47 to 28%) between reduced and oxidized sulfur phases at Gale crater closely resembles that between sulfide and sulfate (-42 to 28%) of the Haughton impact structure in the Canadian High Arctic, interpreted to reflect biological sulfate reduction in an impact-generated hydrothermal system¹⁸. Small amounts (nanomole scale) of OCS and CS_2 that co-evolved with SO_2 and H_2S from Sheepbed samples suggest reactions between sulfur- and carbon-bearing compounds during pyrolysis. The identification of chlorobenzene¹⁹ and possibly sulfonic acids (see Supplementary Information) provides further evidence for the presence of organic compounds at CB, which could be of meteoritic or indigenous Martian origin. Results for the carbon isotopic composition of sulfur-associated carbon at CB are lacking at present. Thus, while sulfur isotopic signatures observed at Gale crater are broadly consistent with those produced by terrestrial microbes, biogenicity should be invoked as a serious possibility only after all potential abiogenic hypotheses have been discounted. This is not the case with our data set, discussed below.

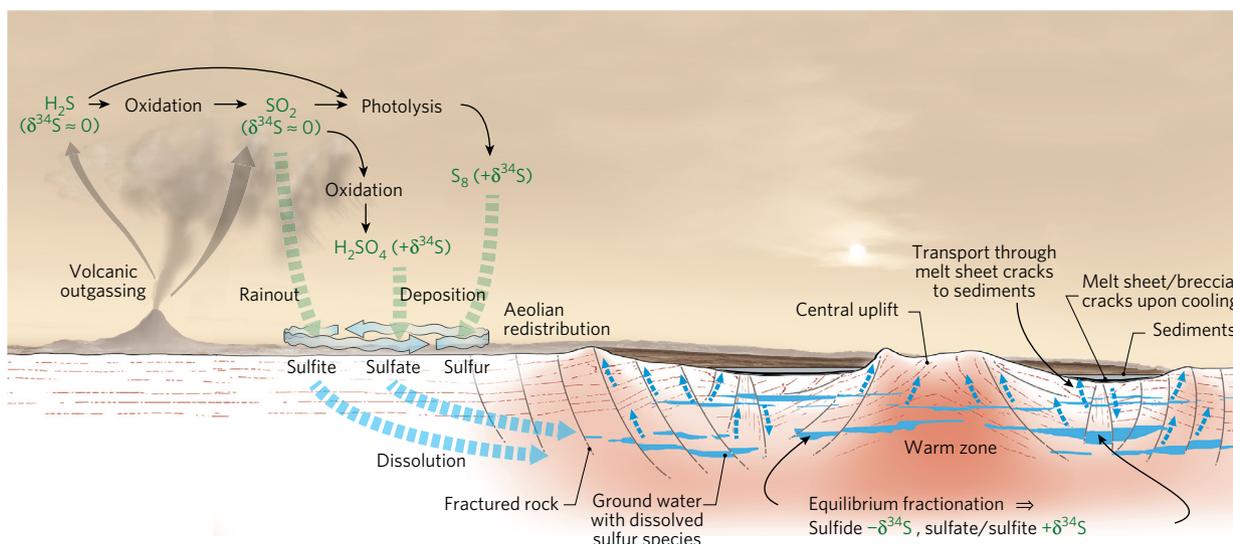


Figure 2 | Conceptual diagram illustrating possible mechanisms for generating and preserving the range of sulfur isotopic fractionations observed.

Fractionation can occur by both hydrothermal processes in the subsurface (blue) and atmospheric processes (green). Atmospheric chemistry shown is not comprehensive but indicates general mechanisms for producing ^{34}S enrichments preserved at the surface. Impact crater characteristics modelled after refs 3,4.

A model for the sulfur isotopic variability at Gale crater

Combined effects of equilibrium isotopic fractionation in groundwater warmed by impact and atmospheric chemical and photochemical processes could generate the observed range of sulfur isotopic compositions without biological activity (depicted in Fig. 2). Studies of terrestrial impact craters suggest that a crater the size of Gale could sustain an impact-driven hydrothermal system for several hundred thousand years^{3,4}. A melt sheet at the crater floor may have been impermeable immediately after impact, and once solidified and cooled, could have formed the base of a crater lake filled by water that discharged through fracture systems around the central uplift or within the crater rim²⁻⁴. Depositional models for the stratigraphy encountered by Curiosity suggest that a fluvio-lacustrine system was active in Gale crater for at least 10^4 to 10^7 years, with individual ephemeral lakes potentially linked by a common groundwater table¹. This system deposited sediments of nominally basaltic composition^{1,14}. If reduced sulfur in clastic sediment were dominated by igneous sulfides, it would have $\delta^{34}\text{S}$ near zero. Depending on the source (for example, weathering of sulfides or SO_2 oxidation), sulfate or sulfite in this material would probably introduce variable ^{34}S enrichments to sediments.

The cooling melt sheet would have formed fractures, allowing percolation of groundwater into overlying sediments²⁻⁴. Pre-existing igneous pyrrhotite and other sulfides dissolved in warm groundwater would have contributed reduced sulfur that mixed with sulfate from surface sources in the hydrothermal system, with pH buffered by other minerals in the rock. Referring to Supplementary Fig. 2, sulfur isotopic equilibrium between sulfide and sulfate could have been reached within several thousand years at 100–150 °C to yield $\Delta^{34}\text{S} \sim 30$ to 40‰, offering a pathway for generation of isotopically depleted sulfides. A similar mechanism involving impact-driven hydrothermalism has been invoked to explain $\delta^{34}\text{S}$ of -9 to -10 ‰ in carbonate-associated pyrites of the ALH 84001 meteorite¹¹. Assuming that sulfide represented a minor phase compared with the more oxidized form of sulfur, the corresponding enrichment in the oxidized phase would be small. Upward migration of fluids that had interacted with this subsurface reservoir during infilling of the crater would introduce isotopically depleted sulfide to overlying sediments.

To account for highly enriched sulfur observed in Gale crater and some meteorites⁶⁻¹², we propose atmospheric processing of SO_2 and H_2S and subsequent incorporation of products into surface sulfate deposits. Broadband UV photolysis experiments with SO_2 have produced elemental sulfur carrying large enrichments in ^{34}S with simultaneous depletions of a few per mil in the residual SO_2 reservoir²⁰. Similar behaviour has been observed in products of H_2S photolysis experiments²¹, suggesting that elemental sulfur produced from photolytic products of either gas would be enriched in ^{34}S . Studies of sulfate in terrestrial volcanic ash have shown that gas-phase oxidation of SO_2 can also produce large fractionations in sulfur isotopes through multiple pathways^{22,23}, including heterogeneous chemistry in atmospheric clouds or in SO_2 and H_2O adsorbed on dust or ash particles^{22,24} as well as homogeneous oxidation of SO_2 by reaction with OH radicals^{22,25}. These oxidative processes could generate fractionations of tens of per mil in sulfate aerosols²⁶.

The atmospheric lifetime of SO_2 is affected by total pressure, composition and redox state of the atmosphere. Modelling of a weakly reducing atmosphere that may have characterized the late Noachian to early Hesperian period (500 mb CO_2 , 100 mb N_2 , and initial SO_2 mixing ratio between 10^{-8} and 10^{-6}) predicted SO_2 lifetimes of hundreds of years or longer, depending on assumptions regarding annual precipitation³. The dominant removal pathway under ancient conditions was SO_2 rainout (almost 90%), with minor contributions from deposition of sulfate ($\sim 10\%$) and elemental sulfur aerosols ($< 1\%$)²⁷.

Regardless of aerosol speciation, some degree of enrichment in ^{34}S would probably have accompanied atmospheric aerosol formation. If SO_2 rainout occurred quickly enough, the SO_2 reservoir would have retained $\delta^{34}\text{S}$ close to zero, with little isotopic fractionation expected during subsequent formation of sulfite minerals. Sulfite and elemental sulfur may have been oxidized to sulfate during later diagenesis, consistent with the predominance of enriched isotopic signatures observed in Martian sulfite and sulfate minerals. Aerosol deposition and SO_2 rainout, followed by incorporation of some SO_2 into sulfite minerals, thus offers a potential mechanism for preserving the fingerprint of atmospheric chemistry in distinct $\delta^{34}\text{S}$ signatures among phases.

The SO₂ evolution temperatures of CB indicate that a large fraction of sulfur in this sample is now oxidized, suggesting oxidation of sulfide by a later diagenetic event. Fluid from this event may have delivered additional sulfur bearing a more enriched isotopic composition, diluting the signal from the depleted sulfide. Differences between δ³⁴S at John Klein (JK) (~0‰) and CB (~−30‰) could derive from local variations in composition of their respective diagenetic fluids or from overprint of an initially depleted signature at JK by isotopically enriched sulfur delivered during one or more later episodes. Differences in smectite structure and abundances of sulfate-filled veins and nodules between JK and CB suggest highly localized diagenetic conditions and greater influence of late-stage sulfate-bearing fluids at JK^{14,15,28}. A small, high-temperature SO₂ peak in OU, with δ³⁴S of $-5 \pm 17\%$, also suggests a separate sulfate phase in this sample, possibly delivered in a later diagenetic event.

As seen in Fig. 1, SO₂ evolved from other samples above Yellowknife Bay showed variable enrichments in ³⁴S, with δ³⁴S from $2 \pm 7\%$ to $28 \pm 7\%$. Although we did not observe depleted isotopic signatures in these samples, it is possible that minor depleted sulfide delivered to some sediments was overwhelmed by a much larger amount of enriched sulfate or sulfite. This could explain the difference in shape and isotopic composition of the low-temperature peak of Mojave (MJ) compared with overlapping peaks at OU and CB. The large ³⁴S enrichments of 20 to 30‰ in several samples suggest a greater fraction of atmospherically processed sulfur in their diagenetic components, indicating influx of fluids compositionally distinct from those that affected CB and OU.

Supporting evidence from Curiosity's payload

Several additional lines of evidence support a history involving multiple diagenetic episodes. Relative abundances of several key elements suggest a history of multiple diagenetic events, with some alteration fluids affecting both Yellowknife Bay and the Murray formation²⁹. Variations in textural properties among sulfates detected throughout Curiosity's traverse support their emplacement during different episodes. For example, Ca sulfates with nodular 'chicken-wire' texture are interpreted as an early diagenetic product in the Sheepbed mudstone that has not been observed in overlying sediments, while a later diagenetic episode produced gypsum, bassanite and anhydrite in veins at other locations¹⁵. A multi-stage process for the diagenetic events at Yellowknife Bay is also suggested from a combination of modelling and analogue work investigating clay formation and the purity of sulfate veins¹⁷. In addition, chlorine isotopic signatures of these samples reveal distinctive compositions for Sheepbed mudstone samples compared with overlying sediments³⁰. Samples of JK and CB produced average δ³⁷Cl of $-11 \pm 7\%$, with those of the Kimberley and Pahrump Hills samples yielding a mean δ³⁷Cl of $-43 \pm 6\%$ (ref. 29). These signatures were interpreted to reflect variable inputs from atmospherically processed chlorine incorporated as oxychlorine or chloride compounds at the surface, similar to the mechanism we propose for producing variable ³⁴S enrichments.

With the context provided by Curiosity's payload suite, these observations offer unprecedented insight into the Martian sulfur cycle, providing evidence for rich hydrothermal sulfur chemistry overprinted by signatures of atmospheric chemistry. As Curiosity continues her journey, the ability to interrogate the Martian sulfur isotope record preserved in the stratigraphic sequence of Mount Sharp will enable evaluation of first-order hypotheses concerning the impact of the sulfur cycle on ancient global climate.

Methods

Methods, including statements of data availability and any associated accession codes and references, are available in the online version of this paper.

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Author contributions

H.B.F. developed analytical methods, calculated and interpreted sulfur isotope ratios, performed calibration experiments, and wrote the manuscript and most of the

Supplementary Information. A.C.M. wrote the mineralogy section of the Supplementary Information. H.B.F., A.C.M. and C.A.K. performed supporting laboratory EGA studies. C.F. contributed to analysis of calibration data. D.L.E. calculated theoretical equilibrium fractionation factors for relevant sulfur-bearing species. H.B.F., J.W.D. and R.P. performed ground-truth isotopic analyses of calibrants. All authors participated in discussion of results and/or editing of the manuscript.

Additional information

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Competing financial interests

The authors declare no competing financial interests.

Methods

Samples of solid Martian materials, each with mass ~ 45 to ~ 135 mg, are analysed through evolved gas analysis (EGA), in which drilled rocks or surface fines are loaded into quartz sample cups for insertion into one of SAM's two pyrolysis ovens. All samples presented here were passed through a $150\ \mu\text{m}$ sieve before loading into the sample cups. After insertion into the oven, samples are heated to $\sim 850\ ^\circ\text{C}$ at a rate of $35\ ^\circ\text{C}\ \text{min}^{-1}$ under 25 mb He pressure, with a model-derived flow rate of 0.8 standard cubic centimetres per minute (sccm). The bottom of each quartz cup contains a porous quartz frit, allowing the He carrier gas to sweep evolved gases from the oven efficiently. During heating, a small split of the gas is directed into the quadrupole mass spectrometer (QMS) for continuous monitoring. The QMS uses an electron impact ionization source and secondary electron multiplier detector, operated in pulse-counting mode³¹. Although the QMS mass range extends from m/z 2 to 535, EGA experiments typically utilize a 'smart-scanning' algorithm designed to optimize dwell time at masses where signal is detected during each run³¹. All data are corrected for detector effects (see the 'Calibration' section of the Supplementary Information) and instrument background prior to quantitative analysis.

The sulfur isotopic composition is nominally calculated from SO_2 produced by thermal degradation and/or oxidation of sulfur-bearing compounds present in the samples. Sulfur isotope ratios are reported with respect to the Vienna Cañon Diablo Troilite (V-CDT) reference³² in delta notation, where $\delta^{34}\text{S} = 10^3 \left[\left(\frac{{}^{34}\text{S}/{}^{32}\text{S}}{\text{sample}} \right) / \left(\frac{{}^{34}\text{S}/{}^{32}\text{S}}{\text{V-CDT}} \right) - 1 \right]$. An extended description of the Methods can be found in the Supplementary Information.

Data availability. All SAM data are available at the Geosciences Node of NASA's Planetary Data System: <http://pds-geosciences.wustl.edu/missions/msl/sam.htm>.

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