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Franz, H. B.; McAdam, A. C.; Ming, D. W.; Freissinet, C.; Mahaffy, P. R.; Eldridge, D. L.; Fischer, W. W.; Grotzinger, J. P.; House, C. H.; Hurowitz, J. A.; McLennan, S. M.; Schwenzer, S. P.; Vaniman, D. T.; Archer, P. D.; Atreya, S. K.; Conrad, P. G.; Dottin III, J. W.; Eigenbrode, J. L.; Farley, K. A.; Glavin, D. P.; Johnson, S. S.; Knudson, C. A.; Morris, R. V.; Navarro-Gonzales, R.; Pavlov, A. A.; Plummer, R.; Rampe, E. B.; Stern, J. C.; Steele, A.; Summons, R. E. and Sutter, B. (2017). Large sulfur isotope fractionations in Martian sediments at Gale crater. *Nature Geoscience*, 10 pp. 658–662.

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Version: Accepted Manuscript

Link(s) to article on publisher's website:
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Large Sulphur Isotope Fractionations in Martian Sediments at Gale Crater

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*Accepted for publication in Nature Geoscience
July 13, 2017*

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Variability in the sulphur isotopic composition in sediments can reflect atmospheric, geological, 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 sulphur-bearing volcanic gases. Here we report in situ analyses of the sulphur 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

sulphur isotopic composition that exceed those measured for Martian meteorites and show both depletion and enrichment in ^{34}S . Measured values of $\delta^{34}\text{S}$ range from $-47 \pm 14\%$ to $28 \pm 7\%$, 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 sulphur isotopic signatures at Gale crater can be explained by equilibrium fractionation between sulphate and sulphide in an impact-driven hydrothermal system and atmospheric processing of sulphur-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 sulphur chemistry for periods lasting several hundred thousand years²⁻⁴. Both atmospheric and geological processes may have produced isotopic variability in sulphur-bearing minerals that is visible today.

Sulphur isotopic signatures are also interesting in astrobiological context, as depletion in heavy isotopes is characteristic of microbial sulphur 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 sulphur 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 traveled ~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. Geological context for these samples is summarized in the Supplementary Information (SI) and depicted in the stratigraphic column of Fig. 1, which also provides sample identities. Here we report highly variable sulphur 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 SI. Sulphur isotope ratios ($\delta^{34}\text{S}$) for these samples are reported in Table S1 and plotted in stratigraphic context in Fig. 1, while SO_2 release profiles are shown in Supplementary Fig. 1. For experiments in which the EGA profile suggests the possibility of more than one sulphur-bearing phase, compositions of multiple phases are reported if possible.

Values of $\delta^{34}\text{S}$ computed for these samples range from $-47 \pm 14\%$ to $28 \pm 7\%$ (1σ), representing statistically significant variability even with consideration of 2σ uncertainties. Notably, SO_2 peaks of the Cumberland (CB) and Oudam (OU) samples reveal significantly ^{34}S -depleted isotopic compositions, while all other samples are close to V-CDT (and Martian mantle sulphur⁶) or enriched in ^{34}S . These new data reveal a much wider range of isotopic fractionation than seen in sulphur-bearing phases of Martian meteorites⁶⁻¹². The igneous lithologies of meteorites have yielded an estimate of the juvenile Martian sulphur composition⁶ and glimpses of atmospherically-processed sulphur incorporated into magmas or as secondary sulphates⁶⁻¹². However, the lack of an efficient sulphur 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 sulphur broaden our perspective on the Martian sulphur cycle by providing direct evidence of reduction-oxidation processes in an environment not previously accessible for exploration.

Sulphur observed at CB and OU, interpreted to derive from sedimentary sulphides, is depleted in ^{34}S by ~30-40‰ compared to Martian igneous sulphides⁶ and by 60-80‰ compared to the most enriched compositions observed in samples of the Murray and Stimson formations. Neither igneous processes nor oxidative weathering of igneous sulphides would cause appreciable fractionation of sulphur isotopes. However, both isotope exchange between oxidized and reduced forms of sulphur and atmospheric processes can generate large fractionations, as can kinetic processes associated with reduction and disproportionation of high- and mid-valence sulphur compounds¹³.

Observations by other Curiosity instruments constrain diagenesis of the Sheepbed mudstone to ~60-80 °C¹⁴ with fluids of circumneutral pH^{14,15}. Supplementary Fig. 2 shows the equilibrium sulphur isotopic fractionation expected between aqueous sulphate/sulphide, sulphite/sulphide, and total bisulphite/sulphide based on theoretical calculations¹⁶ and indicates approximate times required to reach 90% sulphate/sulphide 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 sulphate/sulphide 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 sulphur phases at Gale crater closely resembles that between sulphide and sulphate (-42 to 28‰) of the Haughton impact structure in the Canadian High Arctic, interpreted to reflect biological sulphate reduction in an impact-generated hydrothermal system¹⁸. Small amounts (~nanomoles) of OCS and CS₂ that co-evolved with SO₂ and H₂S from Sheepbed samples suggest reactions between sulphur- and carbon-bearing compounds during pyrolysis. The identification of chlorobenzene¹⁹ and possibly sulphonic acids (see SI) 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 sulphur-associated carbon at CB are presently lacking. Thus while sulphur isotopic signatures observed at Gale crater are broadly consistent with those produced by terrestrial microbes, biogenicity should only be invoked as a serious possibility after all potential abiogenic hypotheses have been discounted. This is not the case with our dataset, discussed below.

A model for the sulphur 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 sulphur 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 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 sulphur in clastic sediment were dominated by igneous sulphides, it would have $\delta^{34}\text{S}$ near zero. Depending on the source (e.g., weathering of sulphides or SO_2 oxidation), sulphate or sulphite in this material would likely 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 sulphides dissolved in warm groundwater would have contributed reduced sulphur that mixed with sulphate from surface sources in the hydrothermal system, with pH buffered by other minerals in the rock. Referring to Fig. S2, sulphur isotopic equilibrium between sulphide and sulphate could have been reached within several thousand years at 100-150 °C to yield $\Delta^{34}\text{S}$ ~30 to 40‰, offering a pathway for generation of isotopically depleted sulphides. 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 sulphide represented a minor phase compared to the more oxidized form of sulphur, 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 sulphide to overlying sediments.

To account for highly-enriched sulphur 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 sulphate deposits. Broadband UV photolysis experiments with SO_2 have produced elemental sulphur carrying large enrichments in ^{34}S with simultaneous depletions of a few per mil in the residual SO_2 reservoir²⁰. Similar behavior has been observed in products of H_2S photolysis experiments²¹, suggesting that elemental sulphur produced from photolytic products of either gas would be enriched in ^{34}S . Studies of sulphate in terrestrial volcanic ash have shown that gas-phase oxidation of SO_2 can also produce large fractionations in sulphur 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 sulphate aerosols²⁶.

The atmospheric lifetime of SO_2 is affected by total pressure, composition, and redox state of the atmosphere. Modeling 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 sulphate (~10%) and elemental sulphur aerosols (< 1%)²⁷.

Regardless of aerosol speciation, some degree of enrichment in ^{34}S would likely 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 sulphite minerals. Sulphite and elemental sulphur may have been oxidized to sulphate during later diagenesis, consistent with the predominance of enriched isotopic signatures observed in Martian sulphite and sulphate minerals. Aerosol deposition and SO_2 rainout, followed by incorporation of some SO_2 into sulphite minerals, thus offers a

potential mechanism for preserving the fingerprint of atmospheric chemistry in distinct $\delta^{34}\text{S}$ signatures among phases.

The SO_2 evolution temperatures of CB indicate that a large fraction of sulphur in this sample is now oxidized, suggesting oxidation of sulphide by a later diagenetic event. Fluid from this event may have delivered additional sulphur bearing a more enriched isotopic composition, diluting the signal from the depleted sulphide. Differences between $\delta^{34}\text{S}$ at John Klein (JK) ($\sim 0\text{‰}$) and CB ($\sim -30\text{‰}$) 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 sulphur delivered during one or more later episodes. Differences in smectite structure and abundances of sulphate-filled veins and nodules between JK and CB suggest highly localized diagenetic conditions and greater influence of late-stage sulphate-bearing fluids at JK^{14,15,28}. A small, high-temperature SO_2 peak in OU, with $\delta^{34}\text{S}$ of $-5 \pm 17\text{‰}$, also suggests a separate sulphate phase in this sample, possibly delivered in a later diagenetic event.

As seen in Fig. 1, SO_2 evolved from other samples above Yellowknife Bay showed variable enrichments in ^{34}S , with $\delta^{34}\text{S}$ from $2 \pm 7\text{‰}$ to $28 \pm 7\text{‰}$. Although we did not observe depleted isotopic signatures in these samples, it is possible that minor depleted sulphide delivered to some sediments was overwhelmed by a much larger amount of enriched sulphate or sulphite. This could explain the difference in shape and isotopic composition of the low-temperature peak of Mojave (MJ) compared to overlapping peaks at OU and CB. The large ^{34}S enrichments of 20 to 30‰ in several samples suggest a greater fraction of atmospherically-processed sulphur 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 sulphates detected throughout Curiosity's traverse support their emplacement during different episodes. For example, Ca-sulphates 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 modeling and analogue work investigating clay formation and the purity of sulphate veins¹⁷. In addition, chlorine isotopic signatures of these samples reveal distinctive compositions for Sheepbed mudstone samples compared to overlying sediments³⁰. Samples of JK and CB produced average $\delta^{37}\text{Cl}$ of $-11 \pm 7\text{‰}$, with those of the Kimberley and Pahrump Hills samples yielding a mean $\delta^{37}\text{Cl}$ of $-43 \pm 6\text{‰}$ 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 ^{34}S enrichments..

With the context provided by Curiosity's payload suite, these observations offer unprecedented insight into the Martian sulphur cycle, providing evidence for rich hydrothermal sulphur chemistry overprinted by signatures of atmospheric chemistry. As Curiosity continues her journey, the ability to interrogate the Martian sulphur isotope record preserved in the

stratigraphic sequence of Mt. Sharp will enable evaluation of first-order hypotheses concerning the impact of the sulphur cycle on ancient global climate.

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Supplementary Information is linked to the online version of the paper at www.nature.com/nature.

Methods

Samples of solid Martian materials, each with mass ~45 to ~135 mg, are analyzed 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 μm sieve before loading into the sample cups. After insertion into the oven, samples are heated to ~850 °C at a rate of 35 °C/min under 25 mb He pressure, with a model-derived flow rate of 0.8 standard cubic centimeters 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 “Calibration” section of SI) and instrument background prior to quantitative analysis.

The sulphur isotopic composition is nominally calculated from SO₂ produced by thermal degradation and/or oxidation of sulphur-bearing compounds present in the samples. Sulphur isotope ratios are reported with respect to the Vienna Cañon Diablo Troilite (V-CDT) reference³² in delta notation, where $\delta^{34}\text{S} = 1000 \cdot [({}^{34}\text{S}/{}^{32}\text{S})_{\text{sample}}/({}^{34}\text{S}/{}^{32}\text{S})_{\text{V-CDT}} - 1]$. An extended description of methods may be found in the SI.

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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Acknowledgments

This work was funded by NASA’s Mars Exploration Program. The authors thank T. B. Griswold for figure production, B. Franz for editorial support, J. Farquhar for manuscript review, J. Farquhar and A. J. Kaufman for facilitating isotopic analyses of calibrants, and the technical team at the NASA GSFC Planetary Environments Laboratory for laboratory support.

Author Contributions: H.B.F. developed analytical methods, calculated and interpreted sulphur isotope ratios, performed calibration experiments, and wrote the manuscript and most of the SI. A.C.M. wrote the mineralogy section of the SI. 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 sulphur-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.

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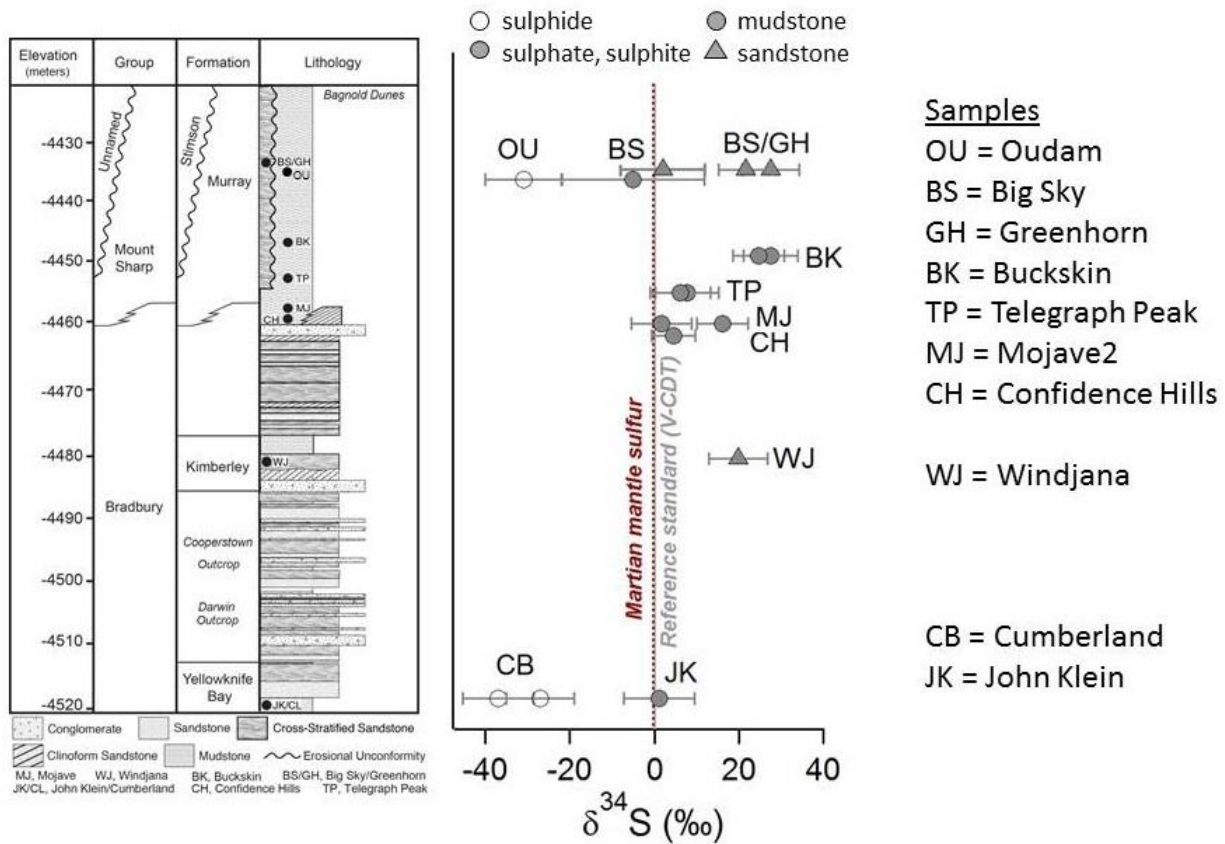


Figure. 1. Measured sulphur isotopic compositions for discrete SO₂ peaks displayed in stratigraphic context. Error bars reflect 1σ uncertainties. Data plotted for the CB sample represent the weighted average of three sample aliquots. Stratigraphic column updated from ref. 1; Martian mantle composition from ref. 8.

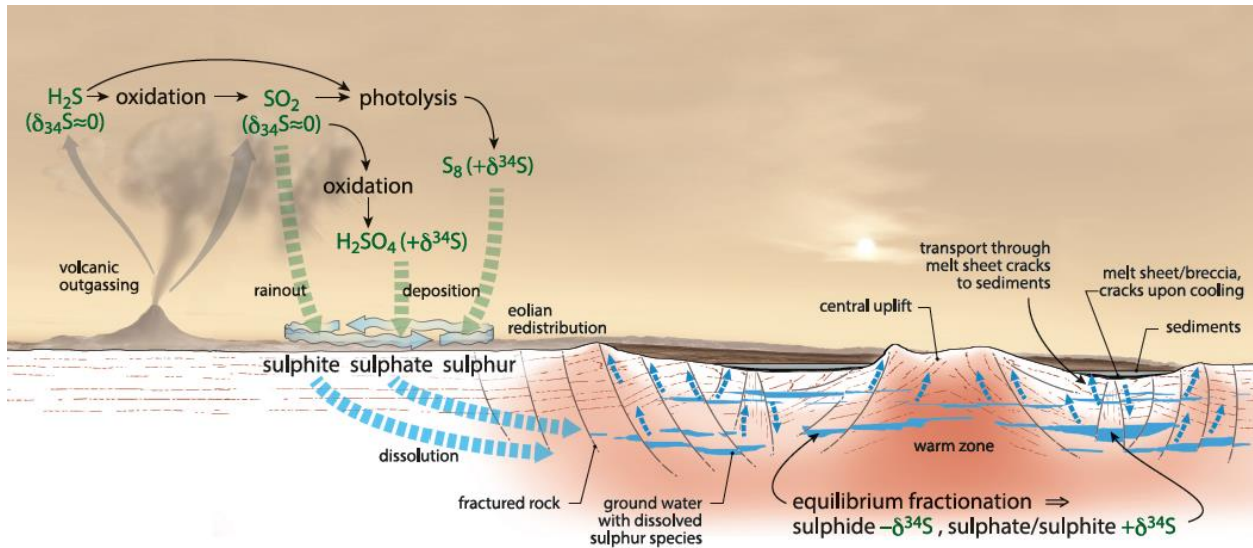


Fig. 2. Conceptual diagram illustrating possible mechanisms for generating and preserving the range of sulphur isotopic fractionations observed. Fractionation can occur by both hydrothermal processes in the subsurface (blue) and atmospheric processes (green). Atmospheric chemistry shown is not comprehensive but indicates general mechanisms for producing ^{34}S enrichments preserved at the surface. Impact crater characteristics modeled after refs. 3, 4.