# SULPHUR ISOTOPE FRACTIONATION IN THE NAKHLITE LAVA FLOWS: NEW INSIGHTS INTO MARTIAN VOLCANIC AND ATMOSPHERIC PROCESSES

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**Introduction:** The sulphur isotopic characteristics of Martian meteorites, including mass independent fractionation, suggest that magmatic assimilation of sulphur occurred throughout the planet's geological history [e.g., 1]. Sulphur isotope ratios can be fractionated by three main processes: hydrothermal [2], photochemical [3, 4], and biological [5]. Large isotopic fractionations of $\delta^{34}S$ (from -47 ± 14 ‰ to 28 ± 7 ‰) have been recently reported using data obtained by the NASA's Curiosity rover along a 13 km long transect in Gale Crater [6]. These sulphur isotopic signatures were interpreted to reflect both equilibrium fractionation in warmed Martian groundwater (low $\delta^{34}S$) and photochemical processes involving $SO_2$ and $H_2S$ (high $\delta^{34}S$) [6; 7, 8]. Building on these findings, we have investigated the sulphur isotope systematics of sulphide grains in five nakhlite meteorites (Nakhla, Lafayette, MIL 090136, Yamato 000749, Yamato 000593), thereby providing new insights into the temporal evolution of volcanic and atmospheric processes on Mars.

**SEM-EDS and Ion Probe Methodology:** Polished thin sections of each sample were chemically mapped and analysed using SEM-EDS at the University of Glasgow. Grains of pyrrhotite and pyrite in these thin sections were then analysed in situ for $\delta^{34}S$, $\delta^{33}S$, and $\Delta^{33}S$ at the Centre de Recherches Pétrographiques et Géochimiques (Nancy, France), using a CAMECA IMS 1280 ion micro-probe.

**$\delta^{34}S$ fractionation results:** Fractionation of $\delta^{34}S$ differs among all five nakhlites. Sulphides in Nakhla, Yamato 000749, and Yamato 000593 have the most convincing magmatic signatures, being characterized by a near zero mean $\delta^{34}S$ (mean -1.67 ± 0.09‰, -1.25 ± 0.10‰, and -1.43 ± 0.06‰, respectively). Conversely, MIL 090136 has an enriched $\delta^{34}S$ (mean +7.28 ± 0.08‰) and the largest intra-meteorite variation in fractionation. This enrichment of $\delta^{34}S$ probably reflects Martian atmospheric processes characterized by oxidation of $H_2SO_4$ or photolysis of $S_8$ due to volcanic eruptions and outgassing [6, 8]; a comparable $\delta^{34}S$ fractionation is recognised in proximity to vents of terrestrial volcanoes (+7.7 ± 0.8‰, [9]). Lafayette shows the greatest depletion of $\delta^{34}S$ yet found in a Martian meteorite (mean -10.8 ± 0.13‰), with $\delta^{34}S$ values attaining -13.25 ± 0.08‰, suggesting equilibrium fractionation in a subsurface groundwater environment. The greater degrees of fractionation of $\delta^{34}S$ that were found by Curiosity are probably due to homogenization of fine crustal materials that have accumulated in Gale Crater over time by fluvial and/or aeolian transport [6]. This process resulted in large and variable fractionation from geographically different areas in comparison to a local series of lava flow units.

**Atmospheric photochemistry on Martian volcanic aerosols:** We compared the nakhlite stratigraphy proposed by [10], which was based on argon isotope geochronology, with our sulphur isotope systematics. This stratigraphic model placed Nakhla and MIL 03346 (paired with MIL 090136) at an intermediate depth in the stack of lava flows, with MIL 03346 older (1390.9 Ma) than Nakhla (1382.5 Ma). Lafayette is likely the uppermost nakhlite lava flow, and the depletion in $\delta^{34}S$ would be indicative of hydrothermally processed sulphur derived by previous atmospheric photolysis enhanced by input of volcanic aerosols. By contrast, MIL 090136 only shows evidence of atmospheric processed sulphur without addition of sulphur isotopic signatures attributable to hydrothermal action. Its enrichment in $\delta^{34}S$ is probably associated with periods of intense input of $SO_2$ and $H_2S$ through volcanic sulphate aerosols. In contrast, Nakhla, along with the two Yamato nakhlites, shows evidence of a dominantly magmatic origin for its sulphur isotopic signatures (near zero $\Delta^{33}S$ and $\delta^{34}S$). Nakhla appears to have spent a significant period of time in contact with the Martian atmosphere (~32 Ma, [10]), a conclusion supported by an excess of $^{17}O$ in this meteorite (atmospheric oxygen component) [11]. Despite this, Nakhla shows only minor $\Delta^{33}S$ and $\delta^{34}S$ fractionation. This minor fractionation can be explained by a long volcanically quiescent period (consistent with a temporal gap), producing much less atmospherically processed sulphur than is evident in MIL 090136, hence preserving the magmatic sulphur signature.

**References:** [1] Franz H. B. et al. (2014) *Nature* 508:364-368. [2] Ohmoto H. and Goldhaber M. B. (1997) *Geochemistry of Hydrothermal Ore Deposits, 3rd ed*. 517 – 611. [3] Zmolek P. et al. (1999) *The Journal of Physical Chemistry* 103:2477-2480. [4] Farquhar J. et al. (2001) *Journal of Geophysical Research* 106:32829-32839. [5] Parnell J. et al. (2010) *Geology* 38:271-274. [6] Franz H. B. et al. (2017) *Nature Geoscience* 10:658-662. [7] Franz H. B. et al. (2013) *Chemical Geology* 362:56-65. [8] Savarino J. (2003) *Geophysical Research Letters* 30:2131. [9] Mather T. A. et al. (2006) *Journal of Geophysical Research* 111:D18205. [10] Cohen B. E. et al. (2017) *Nature Communications* 8:1-9. [11] Farquhar J. et al. (2000) *Nature* 404:50-52.