MYSTERIOUSLY MISSING MARTIAN MIF-S.

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Introduction: The Martian atmosphere is often compared to the Archean Earth's as both are dominated by CO_2-rich and O_2-poor chemistries. Archean Earth rocks preserve mass-independently fractionated sulfur isotopes (MIF-S; non-zero $\Delta^{33}S$), originating from photochemistry in an anoxic atmosphere [1]. Thus, Martian crustal rocks might be expected to preserve non-zero $\Delta^{33}S$. Studies of NWA 7034 (and pairs) – a Martian basaltic breccia – have revealed an anomalous atmospheric MIF-O ($\Delta^{17}O$) signature in metamict zircon, indicating that this regolith sample interacted with the Martian atmosphere-surface environment at 1.5 Ga (middle Amazonian) [2]. This meteorite and its pairs also contain metasomatic pyrite that likely formed in a near-surface regolith setting [3], and thus offers an ideal opportunity to investigate the atmospheric chemistry of Mars through its MIF-S signature.

Methods: We have investigated the sulfide petrogenesis in two pairs of NWA 7034 (NWA 8171 and 11220) and 19 additional Martian meteorites using optical and electron probe-based petrography. SIMS was used to investigate variations in $\Delta^{33}S$ in several of these including NWA 8171. We also conducted LA-ICP-MS on sulfides and chromite in several meteorites to examine their PGE concentrations.

Results: As found previously [3], the basaltic breccia samples contain abundant fine-grained pyrite and almost no pyrrhotite. Amongst the remainder, sulfides (mainly pyrrhotite, minor pentlandite) are most abundant in olivine-phyric, followed by basaltic and poikilitic shergottites. Nakhlites NWA 10720 and MIL 03346 contain ~5 times fewer sulfides than the shergottites. Chassignite NWA 2737 has slightly more abundant sulfides than the nakhlites. In the olivine-phyric shergottites, pyrrhotite is dominantly interstitial. Basaltic shergottites contain pyrrhotite up to 200µm diameter, mainly hosted in the crystal interstices; rare pyrrhotite inclusions in olivine occur in Zagami.

The LA-ICP-MS analyses found that sulfide grains contain insufficient IPGE to be detectable, and very low concentrations of Pd were found in most sulfide grains, and occasionally Pt, Rh and Ru were barely detectable. Of the basaltic shergottites, low PPGE concentrations were only found in NWA 8656.

In basaltic breccia NWA 8171, $\Delta^{33}S$ values for pyrite measured by SIMS range from -0.22 to 0.07 ‰ with an average $\Delta^{33}S$ = -0.12 ± 0.27 ‰, $\delta^{34}S$ values range from -2.34 to 1.02 ‰ with an average of $\delta^{34}S$ = -1.41 ± 0.38 ‰, and $\Delta^{36}S$ values range between -1.46 to +0.40 ‰. Amongst the shergottites NWA 7320, 7397, 8656 and 8716, the calculated averages are $\delta^{34}S$ = -0.31 ± 0.29 ‰ and $\Delta^{33}S$ = -0.02 ± 0.14 ‰.

Discussion: Amongst the shergottites, the basaltic shergottites are the most important for understanding MIF-S because these likely represent lavas that physically interacted with the surface where atmosphere-moderated sulfur-bearing minerals reside. In all basaltic shergottites examined, sulfides are paragenetically late and contain very low PGE indicating low R factor (and thus minimal sulfide-silicate melt interaction), which is consistent with late sulfide saturation. This implies that the lavas did not assimilate surface sulfur, and thus could not inherit a MIF-S signature.

Our S isotope results for basaltic brecca NWA 8171 indicate that it contains no resolvable mass-independent fractionation of S at the 2-sigma level. At first glance this appears to be a surprising result, given that the pyrite clearly formed within the regolith setting from relatively sulfur-rich fluids. But no Martian meteorite yet has yielded a MIF-S signature akin to the large deviations seen on Earth (Fig. 1). We have identified several reasons in addition to that given for the shergottites, why a large MIF-S signature should not be expected on Mars.

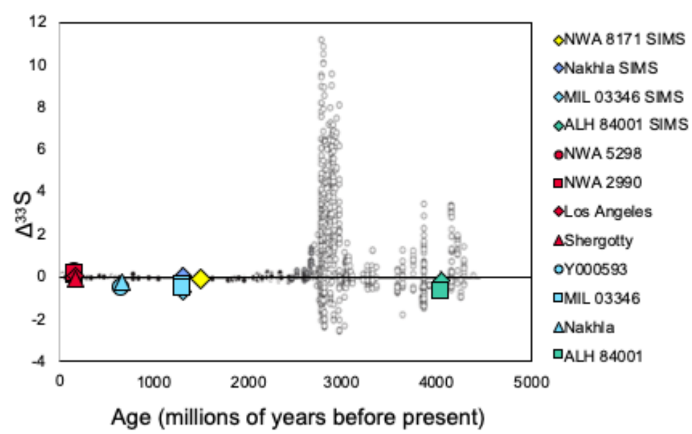

Fig. 1. NWA 8171 (yellow diamond, this study) and anomalous Martian MIF-S analyses (coloured, [1] [4]) compared with the Earth MIF-S record (greyscale points [5].

References: [1] Farquhar J. et al. (2000) *Nature* 404:50-52. [2] Nemchin A. A. et al. (2014) *Nature Geoscience* 7:638-642. [3] Lorand, J.P. et al. (2015) *Meteoritics & Planetary Science* 50:2099-2120. [4] Franz H. B. et al. (2014) *Nature* 508:364-368. [5] Domagal-Goldman, S.D. et al. (2008) *Earth & Planetary Science Letters* 269:29-40.