Evaluating the Role of Sulfate as an Oxidant During the Magmatic History of Paired MIL 03346/090030/090032/090136 Meteorites.

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Paired Martian meteorites MIL 03346, 090030, 090032, 090136 are the most oxidized nakhlites [1]. Franz and others [2] argue the oxidation is a result of the reduction of S^{6+} (from assimilated sulfate) to S^{2-} to form sulfide, and that this may account for the the oxidation of Fe^{2+} (in silicates) to form Fe^{3+} present in magnetite and pyroxene. Here, we test this hypothesis using SIMS to evaluate the sulfur isotopic composition of MIL sulfides and modal analyses to evaluate how much of the Fe^{3+} can be accounted for by sulfate assimilation and reduction. Our ion probe data yield more positive $\delta^{34}S$ values (13.7‰ -14.7‰ ± 2.33‰) and more negative $\Delta^{33}S$ values (-0.60‰ to -0.76‰ ± 0.12‰) for MIL 090030, 090032, 090136 than measured by [2]. However, these values lie on a projection of an array generated by other nakhlite sulfides, including the MIL pairs [2], lending further support to the suggestion that mass-independent sulfur was incorporated into nakhlite melts.

The following two sulfate assimilation reactions: $13FeSiO_3+CaSO_4 \rightleftharpoons FeS+4Fe_3O_4+CaSiO_3+12SiO_2$ and $55Fe_2SiO_4+4KFe_3(OH)_6(SO_4)_2 \rightleftharpoons 8FeS+38Fe_3O_4+55SiO_2 +2K_2O+2H_2O$; yield a volume ratio of magnetite/sulfide of 91.9%/8.1% and 92.2%/7.8%, respectively. We observe a magnetite/sulfide ratio of 94.5 ± 1.4%/5.5 ± 0.3% in (MIL090136). This ratio has too little sulfide to account for the Fe^{3+} in pyroxene (calculated from [3]) and magnetite. Our calculations take into account estimates of sulfide in the precursor melt (estimated from sulfide abundance of Nakhla) and the Ti content of magnetite, which dilutes the Fe^{3+} contained by this mineral. These estimates are lower limits as degassing of sulfur gases during emplacement and also terrestrial weathering of sulfides would reduce the observed FeS abundance compared to the amount of sulfate reduced. These results imply that assimilation of mass-independent sulfate followed by its reduction contributed significantly to the redox variation observed among nakhlites. [1]Udry et al., 2012, ***MPS*** [2] Franz et al., 2014, ***Nature*** [3] Dyar et al., 2005 ***JGR***.