



# Evidence for oxidation at the base of the nakhlite pile by reduction of sulfate salts at the time of lava emplacement

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## Abstract

The assimilation of sulfate by Martian melts could explain the highly oxidized state of some Martian nakhlite meteorites, such as those paired with MIL 03346 (MIL 090030, MIL 090032, and MIL 090136). Here, a combination of new sulfur isotope data, mineral composition and abundance data, and consideration of mineral textures is used to link assimilation of surface-derived Martian sulfate to oxidation of nakhlite melts. The magnitudes of the mass independent sulfur isotope signatures (negative  $\Delta^{33}\text{S}$ ) and the abundance of sulfide minerals accounts for much of the added oxygen implied by the occurrence of abundant skeletal titanomagnetite in the MIL pairs. Assimilation and reduction of sulfate amounts equivalent to that from 10's of centimeters of Martian sediment are required to account for an oxidation front extending  $\sim 1$  m into the flow, a position previously proposed for MIL 03346, and implies a position at the bottom, rather than the top of a nakhlite flow. A similar positional and amount constraint is required for an alternative path for assimilation of sulfate from sulfate-rich brine. Assimilation and reduction of sulfate is therefore inferred to play a critical role in establishing both the enrichment in skeletal titanomagnetite within the lower portion of the nakhlite pile and the large  $\Delta^{33}\text{S}$  anomalies of the MIL pairs. Other nakhlites with smaller  $\Delta^{33}\text{S}$  anomalies and less titanomagnetite would occupy positions farther away from the source of sulfate.  
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## 1. INTRODUCTION

The nakhlite meteorites are clinopyroxene rich cumulates that are thought to originate on Mars in one or more thick volcanic flows of a minimum 15–20 meters thickness (e.g. [Lentz et al., 1999](#)). Cumulus and intercumulus phases are consistent with at least two stages of crystallization. Two hypotheses have been proposed to explain the cumulate minerals: cumulate phenocrysts formed either in a single event in a staging chamber ([Mikouchi et al., 2003](#); [Treiman, 2005](#); [Day et al., 2006](#); [Imae and Ikeda, 2007](#);

[Udry et al., 2012](#); [McCubbin et al., 2013](#); [Richter et al., 2014](#); [Jambon et al., 2016](#); [Richter et al., 2016](#); [Balta et al., 2017](#)) and were then transported and erupted with nakhlite lavas; or, they formed in two stages of melt evolution – the first stage involving high degree silica-poor melts producing olivine, and a second stage yielding augite from an evolving silica-rich melt upon ascent ([Goodrich et al., 2013](#)).

Studies of nakhlites have documented a variable range of oxygen fugacities extending from QFM  $-4$  to QFM  $+1.5$  and suggested changes in oxygen fugacity accompanied their magmatic and post magmatic evolution ([Bunch and Reid, 1975](#); [Dyar et al., 2005](#); [Makishima et al., 2007](#); [Richter et al., 2008](#); [Rutherford and Hammer, 2008](#);

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Treiman and Irving, 2008; McCanta et al., 2009; Szymanski et al., 2010; Richter et al., 2014). Nakhilites also preserve evidence for interactions between nakhilite melts and surface-derived materials: sulfide with anomalous sulfur-isotope signatures as a result of assimilation of surface-derived sulfur (Farquhar et al., 2007; Franz et al., 2014); Cl-rich amphibole due to Cl-rich fluid interaction (Sautter et al., 2006; McCubbin et al., 2013); and isotopically light lithium isotope compositions (1.8–5.2‰) that indicate the presence of crustal contaminants (Magna et al., 2015). Moreover, variable amounts of intercumulus phases formed after crystal-liquid segregation (Dyar et al., 2005; Day et al., 2006; Udry et al., 2012) and intercumulus phases of some nakhilites, such as those from the Miller Range of Antarctica (MIL 090030, MIL 090032, and MIL090036), include abundant skeletal magnetite and silica-rich mesostasis indicative of high oxygen fugacities during the latest stages of their crystallization.

Geochemical and petrologic characteristics of nakhilites have prompted hypotheses about genetic relationships linking them. It is generally believed that the nakhilites derive from different positions within one or more stratigraphically-related flows (Mikouchi et al., 2003; Mikouchi et al., 2006; Richter et al., 2016; Balta et al., 2017; Cohen et al., 2017). The relative positions of various nakhilites within the nakhilite pile and the processes that generated differences in their chemical, isotopic, and mineralogical characteristics, including why some like the MIL pairs became oxidized enough to yield significant amounts of skeletal titanomagnetite as an intercumulus phase, are issues that have not been fully resolved.

Work drawing on cooling rate determinations has led to debate about the position of members of the nakhilite group within the pile. One school of thought orders the nakhilites from most quickly-cooled at the top of the flow (MIL 03346, NWA 817, and Y00593) to more slowly-cooled deeper in the flow (Nakhla, Governador Valdez, Lafayette, and NWA998) (Mikouchi et al., 2006). Richter et al. (2016) use a 1-D thermal cooling model to argue that positions at the top and the bottom of the flow both satisfy fast cooling rates for NWA 817 (0.2 °C/h) and MIL 03346 (1 °C/h). These authors discuss how a mechanism to drain the lava overlying the cumulate layer, such as by the flow breaching its topographical enclosure, is a requirement to allow for efficient heat transfer and cooling for a top-of-flow position. They also discuss how fast cooling of a location near the base of the flow requires a mechanism to transport lavas with ~80% phenocrysts to a cold surface beneath the flow to promote rapid cooling. Richter et al. (2016) argue thus that both locations are allowed, but that additional constraints are needed to distinguish between them. A recent study by Cohen et al. (2017) has added an alternate scenario, argued on the basis of Ar-ages, that the nakhilites come from several different flows in a volcanic pile. According to their age-based reconstruction, MIL 03346 would be lower in the pile than many other nakhilites, but only because it preserves a more ancient age. Considerations for cooling rates and proximity to flow boundaries would still hold, but in this case the parameterization would need to account for the thickness of each distinct flow.

Franz et al. (2014) provide another window into the relationships between nakhilites, arguing that sulfur isotope data for sulfides from the MIL nakhilites indicate a contribution of sulfur from Martian surface sulfates via assimilation and reduction processes that is seen to a lesser extent in other nakhilites they have analyzed. These authors suggest that sulfates were assimilated by an over-riding flow, reacted with the melt, and were reduced to form sulfide that precipitated as minerals. These authors imply a connection between assimilation and oxygen fugacity changes in the melt.

To determine whether sulfate assimilation can account for the oxygen fugacity required to stabilize the high abundance of magnetite observed in some nakhilites, we performed wavelength-dispersive spectroscopy (WDS) analyses of phases in MIL 090030, 090032, and 090,136 (all studied in Franz et al. 2014), and combine these results with site assignments to determine the Fe<sup>3+</sup> content and oxygen fugacity. In addition, we conducted X-ray mapping of these meteorites to determine the modal abundance and the ratio of magnetite to iron sulfide in the MIL pairs. Finally we examined the scale of isotopic variability by carrying out in-situ sulfur isotope analyses of nakhilite sulfides using secondary ion mass spectrometry (SIMS) in thick sections of these MIL pairs.

The sulfur isotope data are used to place constraints on the amounts of sulfate that could have been converted to sulfide via assimilation and reduction. The constraints on sulfate amounts added were, in turn, used to constrain the stratigraphic position of MIL nakhilites. Our observed anomalous sulfide S-isotope compositions suggest the uptake of high amounts of sulfate of which we hypothesize is most likely to occur at the base of the flow from which these meteorites derive.

### 1.1. Sample description

One inch round polished thick sections of MIL 09003043, MIL 09003287, MIL 09013634 allocated by the Meteorite Working Group from the Antarctic meteorite collections were used for this study. These meteorites are paired with the MIL 03346 nakhilite. MIL 090030, 090032, and 090136 are paired with MIL 03346 on the basis of common recovery location, similarities in mineralogy, and the similar petrographic textures of cumulus and intercumulus phases (Day et al., 2006; Hallis and Taylor, 2011; Udry et al., 2012). MIL 03346 is highly oxidized (QFM +1.5; (Dyar et al., 2005); QFM +0.5 (Richter et al., 2008) where QFM refers to log *f*O<sub>2</sub> relative to the Quartz-Fayalite-Magnetite redox buffer) and contains high concentrations of intergranular crystals and interstitial glass (avg. ≈ 24.1% by volume) within the mesostasis (Day et al., 2006; McCanta et al., 2009; Hallis and Taylor, 2011; Udry et al., 2012; Kuebler, 2013). The cumulus phases in all four MIL meteorites are euhedral-subhedral zoned olivine and zoned pyroxene grains with magnesium-rich cores and ferroan rims (Day et al., 2006; Udry et al., 2012). The intercumulus phases are hosted within a glassy matrix and include sodic plagioclase, silica, phosphates, pyroxene, skeletal titanomagnetite, and iron sulfides (Day et al., 2006; Hallis and

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