

## JAROSITE IN A CLINOPYROXENE-HOSTED MELT INCLUSION FROM MARTIAN METEORITE MIL 03346: EVIDENCE FOR HYDROTHERMAL FORMATION BY SULFIDE OXIDATION.

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**Introduction:** Our current view of the martian paleo-climate has been strongly influenced by recent orbital and lander characterization of minerals that have formed in the presence of liquid water [1,2]. As a result, global-scale hypotheses for the evolution of the martian surface have been revisited, and it is now largely agreed upon that acidic fluids played a central role in martian surface geochemistry, forming minerals such as jarosite and other sulfates [1,2]. However, both the temporal evolution and specific formation mechanisms (i.e., hydrothermal, low-temperature, etc.) of many of these unique mineral deposits are under-constrained, and the reconstruction of climatic conditions on Mars over geologic time remains incomplete.

Here, we report the discovery of jarosite formed in a clinopyroxene-hosted melt inclusion of the martian meteorite Miller Range 03346 (Mil 03346). Our findings provide direct evidence that martian magmatic fluids can play an important role in the formation of jarosite. We also present novel evidence that this jarosite has retained textural and geochemical evidence for formation by sulfide oxidation.

Mil 03346 belongs to the Nakhilite class of SNC meteorites believed to have come from Mars. It is a cumulate clinopyroxenite with cumulus clinopyroxene and olivine grains [3-5]. Interstitial to these cumulus grains are skeletal titanomagnetite grains, small fayalitic olivines, chromite, pyrrhotite, cristobalite, apatite, chalcopyrite, and glassy material of variable composition [3-7]. Some of the cumulus grains contain large (~50-100  $\mu\text{m}$ ) melt inclusions.

Jarosite has been found previously within the mesostasis of this meteorite filling small veins and fractures [8]. This jarosite is believed to be the result of aqueous alteration by acidic oxidizing fluids similar to jarosite at Meridiani Planum [1,9]. The mesostasis jarosite ranges in composition from natrojarosite to potassic jarosite [8,10] and is commonly associated with fine-grained goethite. Goethite formation requires liquid water and a low-temperature history (< 100°C). The melt inclusion jarosite; however, is distinctly different from the mesostasis jarosite and may be the first evidence of hydrothermally precipitated jarosite on Mars.

**Results:** Pyroxene-hosted melt inclusions in Mil 03346 occur in two mineralogically distinct populations. One population contains the same phases and

textures that occur interstitially. The second population is characterized by the presence of a Cl-rich amphibole that does not occur within the interstitial regions.

Jarosite was found in a melt inclusion of the second population. It is finely intergrown primarily with hematite  $\pm$  Ti-magnetite; however, in some areas both hematite and goethite are present, forming a complex matrix (Fig.1). Raman spectra of the respective phases are depicted in Fig 2. The jarosite/hematite intergrowth in

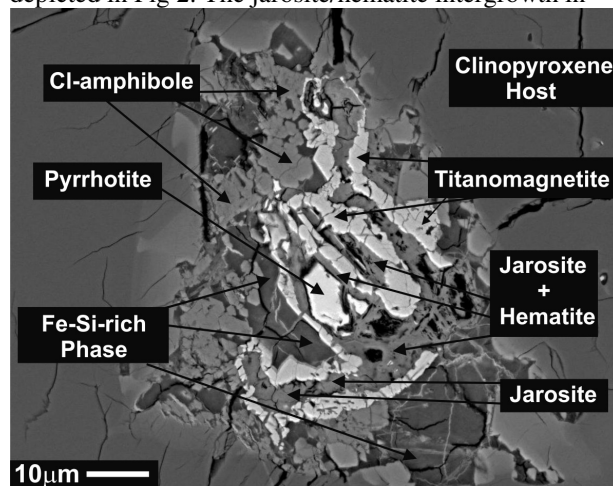


Figure 1. BSE Image of jarosite-bearing clinopyroxene-hosted melt inclusion in MIL03346. All phases identified are labeled.

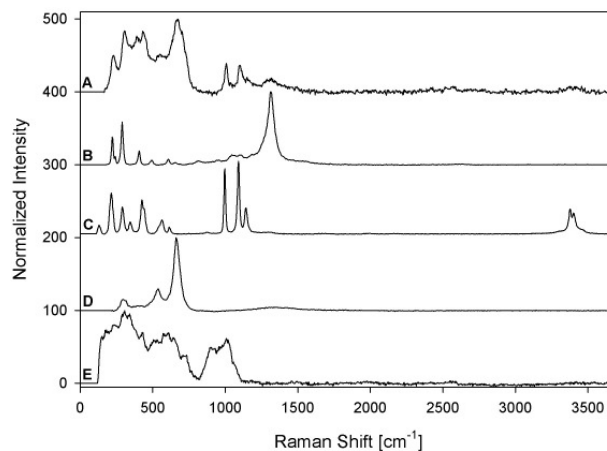


Figure 2. Raman spectra of single phases and phase mixtures within the jarosite-bearing melt inclusion. (A) mixture of jarosite, Ti-magnetite, hematite, and minor goethite (B) Hematite (C) Jarosite (D) Ti-magnetite (E) Fe-Si rich phase. For clarity, the spectra are offset along the y-axis.

the melt inclusion surrounds a magmatic pyrrhotite grain and extends about 10-15 microns beyond the sulfide grain (Figure 1). In addition to jarosite, hematite, goethite, pyrrhotite, and Ti-magnetite, chlorine-rich amphibole and two intergrown Fe-Si-rich phases containing very small ( $< 1 \mu\text{m}$ ) apatite grains have been identified within the melt inclusion. The Fe-Si-rich phases are more potassic than sodic, and fairly rich in magnesium and aluminum. The primary difference between the two phases is their chemical composition (numbers in parentheses are in Wt.%): Phase 1 has  $\text{SiO}_2$  (45.30),  $\text{TiO}_2$  (0.19),  $\text{Al}_2\text{O}_3$  (8.76),  $\text{Cr}_2\text{O}_3$  (0.02),  $\text{Fe}_2\text{O}_3$  (28.78),  $\text{MnO}$  (0.23),  $\text{MgO}$  (1.71),  $\text{CaO}$  (2.00),  $\text{Na}_2\text{O}$  (0.18),  $\text{K}_2\text{O}$  (1.19),  $\text{P}_2\text{O}_5$  (3.60),  $\text{SO}_3$  (0.86); Phase 2 has  $\text{SiO}_2$  (45.34),  $\text{TiO}_2$  (0.07),  $\text{Al}_2\text{O}_3$  (3.62),  $\text{Cr}_2\text{O}_3$  (0.02),  $\text{Fe}_2\text{O}_3$  (38.82),  $\text{MnO}$  (0.14),  $\text{MgO}$  (2.68),  $\text{CaO}$  (0.65),  $\text{Na}_2\text{O}$  (0.07),  $\text{K}_2\text{O}$  (0.76),  $\text{P}_2\text{O}_5$  (0.15),  $\text{SO}_3$  (0.76)

EPMA analysis of the jarosite [ $\text{A}_1\text{M}_3\text{T}_2\text{O}_8\text{X}_6$ ] confirmed that the A-site is predominately potassic with minor natrojarosite component (0.84 K and 0.18 Na structural formula units (sfu), respectively). The analysis indicates no hydronium component in the jarosite because the A-site is completely filled with potassium and sodium. The computed T-sites occupancies are dominated by sulfate (1.92 sfu); however, there is also substantial phosphate substitution within the site (0.10 sfu). The M-sites are dominated by ferric iron (2.85 sfu) with some aluminum (0.10 sfu) and minor magnesium, chromium, and manganese ( $\text{Mg}+\text{Cr}+\text{Mn} = 0.05$  sfu). The X-sites are likely dominated by hydroxyl, with some chlorine substitution.

**Discussion:** Jarosite precipitation within a melt inclusion requires the presence of an aqueous phase. The infiltrating fluid of meteoric or magmatic origin from outside of the pyroxene host could have been introduced into the melt inclusion after its integrity (i.e. seal) was disturbed. Alternatively, magmatic fluids could have been produced from the trapped melt within the inclusion during crystallization and/or decompression. This fluid phase would remain trapped within the host as long as the melt inclusion remained sealed throughout the magmatic and hydrothermal temperature regimes.

Melt inclusions within hosts such as clinopyroxene with well-defined cleavage, are fairly susceptible to rupture due to their overall lower tensile strength relative to cleavage-free hosts [11]. Therefore, analysis of melt inclusion integrity and assessment of the stage at which such inclusions might have leaked takes on significant importance in this study. There are two distinct populations of large melt inclusions within MIL 03346. Of greatest abundance are melt inclusions containing phases texturally and mineralogically similar or identical to those within the mesostasis. These characteristics

are to be expected for breached melt inclusions that have had early access to the interstitial areas and have seen the same physico-chemical conditions and undergone the same crystallization and alteration processes as the mesostasis. The melt inclusions that are texturally and mineralogically distinct from the mesostasis are thus more likely to represent melt pockets that have remained isolated through their igneous and hydrothermal histories. The presence of Cl-rich amphibole further strengthens this argument since this type of amphibole typically forms from hydrothermal fluids below the solidus temperature of the silicate melt [e.g., 13]. If these melt inclusions had been breached, fluid exsolving from the melt during crystallization would likely have migrated away from the melt inclusions along fractures and therefore, not be available for formation of a hydrothermal mineral assemblage. The jarosite, however, forms at lower temperatures than the Cl-amphibole and its presence could still be supported by late infiltration of meteoric water. Nonetheless, the differences between the composition of the melt inclusion jarosite and the vein jarosite studied previously suggest a significantly different fluid chemistry, one that may have been provided by a sealed melt inclusion. Moreover, the chemical composition of the jarosite mimics those of the Fe-Si phases present within the same melt inclusion, such as elevated  $\text{PO}_4$  contents, high K/Na ratios and measurable Cl.

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