POSSIBLE CAUSES FOR LATE-STAGE REACTION TEXTURES ASSOCIATED WITH PYROXFERROITE AND METASTABLE PYROXENES IN THE BASALTIC MARTIAN METEORITES.
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Introduction: Late-stage mineral assemblages have been reported in the basaltic martian meteorites [1]. These late-stage assemblages show a variety of minerals, including oxides, sulfides and phosphates. In addition, areas of mesostasis are present, typically in abundance from 1-10 wt%.

Of interest are late-stage mineral assemblages that are the result of pyroxferroite and/or metastable pyroxene breakdown. These have been well examined and cataloged in martian meteorite Los Angeles [2]. Pyroxferroite is a pyroxenoid mineral that was first discovered in low pressure lunar rocks [3]. It is metastable at low pressures and breaks down to hedenbergite+fayalite+SiO2 [4]. The purpose of this study is to examine the breakdown products, associated reaction rims, and similar mineral assemblages, in order to better understand their conditions of formation, and the crystallization and cooling histories of the martian basalts that contain these assemblages.

Analytical Method: Thin sections were examined using a JOEL 5800LV scanning electron microscope (SEM) with an attached Oxford Isis Series 300 energy dispersive analytical system, at the Institute of Meteoritics at the University of New Mexico. This instrumentation was used in imaging the following thin sections: QUE 94201,6 (NASA Johnson Space Center), Shergotty UNM 411 and Zagami UNM 991 (University of New Mexico), and Los Angeles, Stone 1 #751 (University of California- Los Angeles). The samples were analyzed with the SEM at an acceleration voltage of 20kV, sample current of 20nA, spot size of 12µm, and a working distance of 12mm.

Observations: Los Angeles, QUE 94201, Shergotty and Zagami have comparable amounts of the Ca-phosphate whitlockite and mesostasis volume percents while their J/O2 and Mg#’s contrast (table 1).

Overall, the late-stage mineral assemblages of the four observed meteorites consistently show oxide minerals such as ilmenite and spinel, iron sulfides, phosphates including whitlockite and chlorapatite, and areas of mesostasis. By examining these late-stage minerals, we were able to locate areas of pyroxferroite/metastable pyroxene breakdown products in three of the four studied meteorites. Meteorites Los Angeles, QUE 94201, and Shergotty all exhibit pyroxferroite/metastable pyroxene breakdown textures, most often adjacent to whitlockite. However, we do not see these breakdown textures associated with apatite.

Observations of the martian basalts are illustrated by SEM images in figures 1-4. Los Angeles (fig. 1), shows pyroxferroite/metastable pyroxene breakdown around an elongate whitlockite grain. A coarsening in the texture in direct contact with the phosphate is observed and is composed of fayalite+SiO2; moving away from the phosphate, the texture is finer and all three pyroxferroite breakdown phases are present (hedenbergite+fayalite+SiO2). Los Angeles contains numerous areas of breakdown textures throughout the analyzed sample. These assemblages are also present adjacent to some areas of mesostasis.

QUE 94201 (fig. 2), also shows breakdown textures commonly throughout the meteorite. In some instances, whitlockite grains are rimmed with fayalite+SiO2; and (hedenbergite+fayalite+SiO2) is not observed. Most frequently, pyroxferroite/metastable pyroxene breakdown products are found rimming one or more sides of a whitlockite grain and contain a textural zoning similar to those observed in Los Angeles.

Shergotty, (fig. 3) in which pyroxferroite breakdown products were not previously reported, shows textures similar to Los Angeles, with coarse to fine textural zoning as well as the absence of the Ca-rich pyroxene phase adjacent to whitlockite. Although reaction assemblages are not seen as consistently throughout the meteorite, Shergotty displays textures very similar to those in Los Angeles and QUE 94201.

In contrast to the three meteorites discussed above, Zagami (fig. 4) shows no signs of pyroxferroite breakdown or associated textures. Whitlockite grains and mesostasis are present in a similar abundance to those in the other meteorites (table 1).

Discussion: The observed textures adjacent to whitlockite and mesostasis are not consistent with simple breakdown of pyroxferroite. We suggest a two-stage history for these textures, involving breakdown of metastable pyroxene and possibly pyroxferroite into fayalite+hedenbergite+SiO2, followed by (or concurrent with) diffusion of calcium.

At 1 bar pressure, certain pyroxene compositions are not stable, including ferrosilite (FeSiO3) and pyroxferroite (Ca12Fe6Si24O70) [4]. As the crystallizing pyroxenes in the martian basalts zoned to an iron rich end member, they may have entered the "forbidden zone" in the pyroxene quadrilateral, and broke down to the stable assemblage hedenbergite+fayalite+SiO2 [5]. This is supported by the observation of stable pyroxenes directly adjacent to breakdown products. The
breakdown assemblages observed in the martian basalts are therefore likely a product of metastable pyroxenes approaching an equilibrium assemblage.

Breakdown products of pyroxferroite or metastable pyroxene have been observed in association with phosphate minerals such as whitlockite as well as areas of mesostasis. This implies that the breakdown textures occurred during the cooling stages of the rock. In general, breakdown is found in direct contact with whitlockite crystals and displays a symplectitic intergrowth texture; observed in some metamorphic rocks as coronal structures. In metamorphic rocks, these textures are caused by diffusion controlled reactions associated with chemical potential gradients [6]. It may be possible that the presence of the Ca-phosphate whitlockite sets up a calcium diffusion gradient allowing for the chemical potentials of Ca, Mg, Fe, and Si to permit elemental exchange while recrystallization/breakdown is taking place. This would explain the presence of pyroxferroite breakdown products closely associated with whitlockite.

Differences in conditions of formation (e.g. Mg#, oxygen fugacity, and cooling rate) may account for the presence or lack of pyroxferroite/metastable pyroxene breakdown products. The lack of these assemblages in Zagami, indicates that it cooled more quickly than the other observed basalts, at least through the temperature range of formation of breakdown products. Alternatively, the higher Mg# of Zagami suggests that a smaller amount of zoned pyroxenes crystalized metastably in the “forbidden zone”. In addition, reheating by shock events or other igneous intrusions may account for these observed reaction textures.


| Table 1. Comparison of martian basalts in this study |
|----------------|----------------|----------------|----------------|
| Sample         | % Whitlockite  | % Mesostasis   | Mg#            | fO2             |
| QUE 94201      | 3.9            | 4              | 0.38           | QFM-3           |
| Los Angeles    | 1.7            | ~5-10          | 0.23           | QFM-1           |
| Shergotty      | ~1             | ~3             | 0.46           | QFM-1           |
| Zagami         | ~0.5           | ~2             | 0.52           | QFM-1           |

Data after [2], [7], [8]; Mg# = Mg/(Mg+Fe)