Symplectites derived from metastable phases in martian basaltic meteorites

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ABSTRACT

The martian basalts Los Angeles, QUE 94201, Shergotty, and Zagami contain several late-stage mineral types including oxides, sulfides, phosphates, and associated silicate assemblages. Symplectites consisting of two- and three-phase assemblages are present in Los Angeles, QUE 94201, and Shergotty. The three-phase symplectite is composed of hedenbergitic pyroxene, fayalitic olivine, and an SiO₂ polymorph, and the two-phase symplectite consists of fayalitic olivine and an SiO₂ polymorph. These symplectites are commonly found in close association with the Ca-phosphate merrillite [general formula Ca₉(Mg,Fe²⁺)(PO₄)₇]. Scanning Electron Microscopy was used to examine the distribution and occurrence of the symplectites, and point-count and electron-microprobe data were used to recast symplectites in terms of pyroxene stoichiometry. The reconstructed three-phase symplectite compositions plot close to lunar (metastable) pyroxferroite on the pyroxene quadrilateral diagram and indicate that pyroxene compositions ranged into the “forbidden region” and eventually crystallized pyroxferroite, which subsequently broke down to the three-phase symplectite upon cooling. Two-phase symplectites, which occur directly adjacent to merrillite, may be the result of breakdown of metastable ferrosilite. The crystal chemistry of merrillite and its close association with the symplectites indicates that during crystallization of pyroxene, co-crystallizing merrillite contributes to depletion of Ca and Mg and the formation of metastable pyroxferroite and ferrosilite.

INTRODUCTION

Pyroxene is typically the first mineral to crystallize in the basaltic shergottite meteorites (herein referred to as martian basalts) (McSween 1994) and continues to form throughout their crystallization histories. As such, pyroxene records changes in melt composition into the final stages of crystallization (Bence and Papike 1972). Late-stage pyroxenes become more Fe-rich and can zone into a metastable region of the pyroxene quadrilateral referred to as the “forbidden region” (Lindsley 1983). Given sufficient metastable crystallization, pyroxferroite, (Ca₁/₇Fe⁶/₇)SiO₃, can form.

Pyroxferroite is a pyroxenoid mineral that was first discovered in low-pressure lunar basalts (Lindsley et al. 1972), although its existence had been previously predicted (Burnham 1971). Synthetic pyroxferroite has the formula (Ca₁/₇Fe⁶/₇)SiO₃, corresponding to Wo₁₄En₁₃Fs₈₆ when recast in terms of pyroxene stoichiometry. Experimental studies show that pyroxferroite is only stable above 10 kbars of pressure (Lindsley and Burnham 1970). However, the mineral can exist metastably at low pressures as observed in lunar mare basalts (Lindsley et al. 1972). Because mare basalts demonstrably crystallized at low pressures, lunar pyroxferroite formed metastably by rapid crystallization and was preserved by rapid cooling (Lindsley and Burnham 1970). Lindsley et al. (1972) confirmed the metastable nature of lunar pyroxferroite with heating experiments.

They found that upon slow cooling (>990 °C for approximately three days), lunar pyroxferroite breaks down to the three-phase assemblage hedenbergitic pyroxene (Hed), fayalitic olivine (Fay), and a silica phase (SiO₂, typically tridymite).

The crystal structure of lunar pyroxferroite was studied by Burnham (1971), who discovered that, in contrast to the idealized pyroxferroite formula in which Ca fully occupies one of the seven M sites [i.e., (Ca₁/₇Fe⁶/₇)SiO₃], in fact, Ca partially occupies three of the seven M sites. This high degree of Ca disorder in the pyroxferroite structure suggests that pyroxferroite with more Ca-rich compositions is possible. However, none has been reported in nature. In terms of Mg content, the crystal structure allows for some substitution of Mg for Fe, although the exact limits of this substitution are unknown (Burnham 1971). Substitution of Mg is evidenced by the composition of lunar pyroxferroite, which ranges (in terms of pyroxene stoichiometry) from nearly Mg-free, Wo₁₃En₁₃Fs₈₆, (Papike et al. 1998) to Wo₁₃En₁₃Fs₇₅ (Boyd and Smith 1971). As these are the only pyroxferroite compositions reported in nature, we will use this range in assessing whether three-phase (Hed + Fay + SiO₂) symplectites found in martian basalts represent pyroxferroite breakdown products. However, we note that more Ca-rich compositions are possible.

In contrast to lunar samples, no metastable pyroxferroite has been found in martian basalts. Pyroxferroite was reported in QUE 94201 by Mikouchi et al. (1998, their Table 1). However, the criteria for distinguishing the grain as pyroxferroite were not stated, and its composition (Wo₁₃En₁₃Fs₈₆) is too Ca-rich to be termed pyroxferroite. Minute grains of pyroxferroite inside maskelynite were reported in Shergotty (Smith and Hervig 1979). However, these authors admit that the grains are