EXPERIMENTAL INVESTIGATION OF SPINEL-PYROXENE SYMPLECTITE FORMATION IN ULTRAMAFIC PLANETARY MATERIALS

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Introduction: Spinel-pyroxene symplectites are vermicular intergrowths containing spinel of varying composition and either high- or low-Ca pyroxene or both, found within a wide range of rock compositions and textures, in terrestrial and extraterrestrial materials. Chromite-pyroxene symplectites have been identified in olivine-bearing lunar rocks [1,2], the ungrouped achondrite Queen Alexandria Range (QUE) 93148 [3], harzburgite inclusions within howardites [4], and most recently ultramafic achondrites Northwest Africa (NWA) 12217, 12319, and 12562, associated with the HED parent body [5].

The formation conditions of symplectites remain enigmatic after many decades of research in numerous petrogenetic regimes. Spinel-pyroxene symplectites have been suggested to form through a reaction between olivine and plagioclase, the diffusion of minor elements out of olivine, the breakdown of preexisting garnet due to changes in pressure and temperature, and the crystallization of a late-stage melt [1,6]. As the provenance of symplectites in planetary materials often defies these constraints, other hypotheses include a reaction with a chromium-rich metasomatic fluid [2] and crystallization from a chromium-rich metal-sulfide melt [4].

The chromite-pyroxene symplectites identified in ultramafic achondrites, harzburgite inclusions within howardites, and QUE 93148 overlap in major element compositional range. As garnet is not a stable phase in these lithologies at low pressure (i.e. small planetary diameter) conditions, its breakdown is not a plausible formation mechanism. Likewise, the chromium requirements of these symplectites rule out diffusion from major phases which contain chromium at trace levels (<0.1 wt.%). Finally, feldspar is not found to be associated with symplectites, and they occur randomly throughout these rocks, sometimes within veins (Fig. 1). Rather, the morphology of chromite-pyroxene symplectites within ultramafic rocks from small bodies suggests formation via late-stage melt or fluid interaction, and our experimental campaign is designed to test this hypothesis.

1-Atmosphere Experiments: All experiments were conducted at the Experimental Studies of Planetary Materials laboratory at Washington University. Bulk starting compositions for experimental materials were based on modeled bulk compositions of the symplectites found within the ultramafic

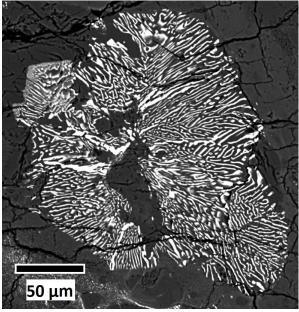


Figure 1. Backscattered electron (BSE) image of chromite-pyroxene symplectite assemblage in ultramafic achondrite NWA 12217. High- and low-Ca pyroxene occurs interstitially to chromite, the bright phase.

achondrites. Electron microprobe point analyses of chromite, low-CA pyroxene, and high-Ca pyroxene components of symplectite returned roughly uniform compositions, while broad-beam analyses of the entire, multi-phase assemblages showed varying Ca content. This suggests that the compositional diversity of the symplectites is due to differences in the ratios of the two pyroxenes. Thus, two synthetic bulk compositions were used in experiments, a high-Ca and low-Ca endmember that simulate the full range of symplectite bulk composition. Starting materials for experiments were synthesized using high-purity silicate and oxide powders.

Experimental charges were heated to examine partial melt compositions using a 1-atmosphere gas mixing furnace operating at an oxygen fugacity (fO_2) one log unit below the iron-wüstite buffer (IW-1). Partial melting was not observed in either composition below 1400° C. This temperature far exceeds the liquidus temperature of a basalt in equilibrium with the Fo₇₃₋₉₃ olivine in these cumulates. These results indicate that the symplectites observed in ultramafic achondrites do not result from the crystallization of a melt with their

composition. The solidus of these symplectites is well

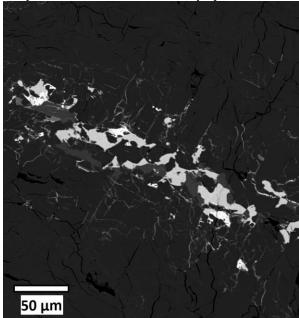


Figure 2. BSE image of a vein in NWA 12217 that is found associated with symplectites. Phases are, in ascending order of brightness, olivine, low-Ca pyroxene, high-Ca pyroxene, chromite, Fe-sulfide.

above that of their host dunite, lherzolite, and harzburgite rocks, such that melting them slightly would substantially melt their host as well. Instead, the melt that the symplectites formed from must have had components that lowered its melting temperature below the solidus of its host rocks and allowed it to percolate through them as veins and conduits (Fig. 2).

Piston Cylinder Experiments: As symplectites are often associated with sulfides in the ultramafic achondrites, it is possible that they crystallized from a lower temperature Fe-Ni-S eutectic melt that percolated through its host rocks and left the symplectites behind. Such a "metallic" melt is better able to account for the high amount of Cr in the symplectites, as silicate melts at low fO_2 are unable to support more than ~1 wt.% of Cr [2,4]. To investigate this possibility, 4.5 wt.% sulfur was added to the experimental compositions as FeS powder, the maximum amount that could be accommodated without affecting the Fe content. All of this sulfur was lost in preliminary 1-atmosphere experiments, indicating the need for confining pressure to prevent volatilization.

The sulfide-enriched experimental powders were loaded into graphite capsules to constrain the fO_2 at or below the C-CO buffer. These charges were brought to 1300 and 1400° C at 1 GPa inside a piston cylinder apparatus to examine partial melting compositions. The bulk compositions of the experimental products were

then analyzed using electron microprobe point analyses of individual phases and scanning electron microscope (SEM) BSE mapping combined with threshold analysis using ImageJ. Compared to the original powders, experimental run products lost 34-54 wt.% S, 21-36 wt.% FeO, 12-28 wt.% Fe, and 4-18 wt.% Cr. One possibility is that initial low viscosity FeS melts were generated but lost through cracks in the graphite capsules. Fe-Sulfide grains that contained up to 14 wt.% Cr were observed throughout the samples, indicating that Cr is a compatible element within sulfides at these conditions. Additional experiments designed to better confine potential S-rich melts are currently underway.

References: [1] Bell P. M. et al. (1975) *Proc. Lunar Sci. Conf.* 6th, 231-248. [2] Elardo S. M. et al. (2012) *GCA* 87, 154-177. [3] Goodrich C. A. and Righter K. (2000) *Met. & Planet. Sci.* 35, 521-535. [4] Hahn T. M. et al. (2017) *Met. & Planet. Sci.* 1-33. [5] Vaci. Z. et al. (2021) *Nat. Comm.* 12:5443. [6] Dawson J. B. and Smith J. V. (1975) *Phys. & Chem. Of the Earth* 9, 339-350