

LATE-STAGE OXIDATION OF YAMATO 980459 SHERGOTTITE: EVIDENCE FROM CHROMITE + SILICA TRAILS IN OLIVINE. S. Che¹, A. J. Brearley¹, and C. K. Shearer^{1,2}, ¹Department of Earth and Planetary Sciences, ¹University of New Mexico, Albuquerque, NM 87131, USA (shaofanche@unm.edu; brearley@unm.edu), ²Institute of Meteoritics, ¹University of New Mexico, Albuquerque, NM 87131, USA (cshearer@unm.edu).

Introduction: Melt characteristics preserved in shergottite olivine provide important information about the magmatic history of the Mars. For example, previous studies on trace element and hydrogen isotopic compositions of melt inclusions trapped in olivine have revealed possible interactions between the Martian mantle and crust [e.g., 1-2]. We previously reported chromite and melt inclusion trails in olivine megacrysts from Yamato 980459 (Y-98), a sample believed to represent a near-primary Martian melt [3]. Here we present additional microstructural and microchemical results, with the goal of reconstructing the magmatic and subsolidus redox history of Y-98.

Methodology: Acquisition of backscattered electron (BSE) images and preparation of focused ion beam (FIB) sections were conducted using a FEI Quanta 3D FEG-SEM/FIB instrument. The extracted FIB sections were then characterized on a JEOL 2010F FASTEM field emission gun scanning transmission electron microscope (STEM/TEM) operated at 200 kV. Quantitative wavelength dispersive spectrometry (WDS) X-ray maps of minor elements were obtained on a JEOL JXA-8200 electron probe microanalyzer (EPMA) using a beam current of 500 nA, a spot size of <1 micron, an accelerating voltage of 15 kV, and a dwell time of 700 ms.

Results: The chromite and melt inclusion trails are observed in the inner region of olivine megacrysts. Chromite is fine-grained (<1 μm) and has euhedral-to-subhedral shapes. BSE images show many of the chromite grains are associated with regions of silica that are <1 μm in size. Quantitative X-ray maps (Fig. 1) illustrate that the trails have enrichments in P and often crosscut the P-zoning pattern of olivine. To investigate the microstructures of the trails, we extracted a FIB section (Fig. 2) from the olivine grain shown in Fig. 1.

Bright-field TEM (BF-TEM) images (Fig. 3a-b) show that chromite grains are typically ~500 nm in size and are closely associated with silica. Silica partially encloses chromite or occurs as thin layers (<50 nm in thickness) around chromite grains. Fractures that connect adjacent chromite + silica have been observed (Fig. 3b). High-resolution TEM (HRTEM) analysis demonstrates that silica is amorphous: Fast Fourier Transformation (FFT) analysis shows a diffuse ring pattern (Fig. 3c). We also investigated the crystallographic relationship between olivine and chromite, when the two phases are in direct contact; however, no

orientation relationship is observed based on HRTEM images (Fig. 3d). The EDS analytical data show that silica contains ~97.4 wt% SiO_2 , ~1.1 wt% MgO, and ~1.0 wt% FeO. The CaO and Al_2O_3 contents are both below 0.5 wt%. The composition of olivine varies with the distance from the trail: elevated Cr_2O_3 contents (up to 1.2 wt%) and higher Mg# (up to 78.5) are observed within a ~300 nm distance from the trail, which drop abruptly to the bulk composition of olivine adjacent to the trail (~0.2 wt% Cr_2O_3 and ~74.3 Mg#). These EDS compositions of the bulk olivine are consistent with previous EPMA data [e.g., 4].

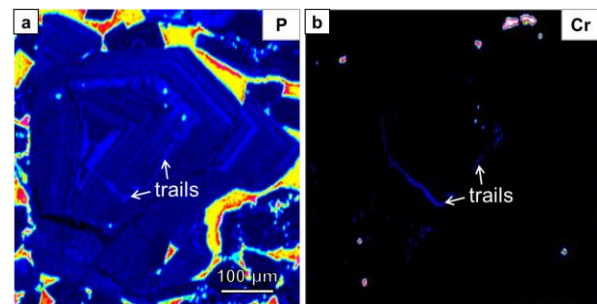


Fig. 1. WDS P and Cr X-ray maps of an olivine megacryst in Y-98. The trails arrowed show P enrichments.

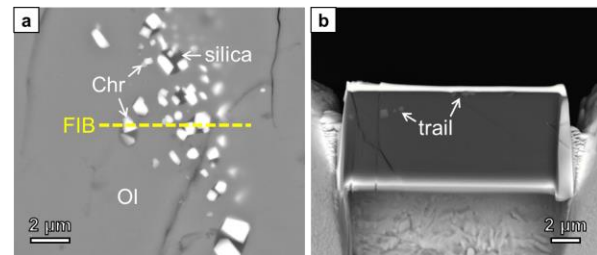


Fig. 2. BSE images of a chromite (Chr) + silica trail in olivine (Ol). In the FIB section, the trail is inclined to the thin section surface.

It has been suggested that some Cr-rich symplectites in shergottite olivine could have formed by exsolution of Cr^{3+} from olivine [e.g., 5]. We therefore lifted out a second FIB section from another olivine megacryst that is free of chromite inclusions to investigate potential Cr-rich exsolution features. However, no evidence of chromite is observed at any scale in either BF-TEM or HRTEM images.

Discussion: In our previous study [3], we discussed several possible mechanisms for the origin of the trails. Our TEM observations provide further evidence against a subsolidus exsolution origin. Chromite and olivine in the FIB section do not show a crystallo-

graphic orientation relationship. However, elongate chromite grains in the trails are sometimes aligned, which suggests they might have an orientation relationship with olivine. The olivine grain that is free of chromite inclusions on the SEM scale does not contain chromite or Cr-rich exsolution lamellae under TEM. This implies that Cr^{3+} exsolution in Y-78 olivine megacrysts did not occur.

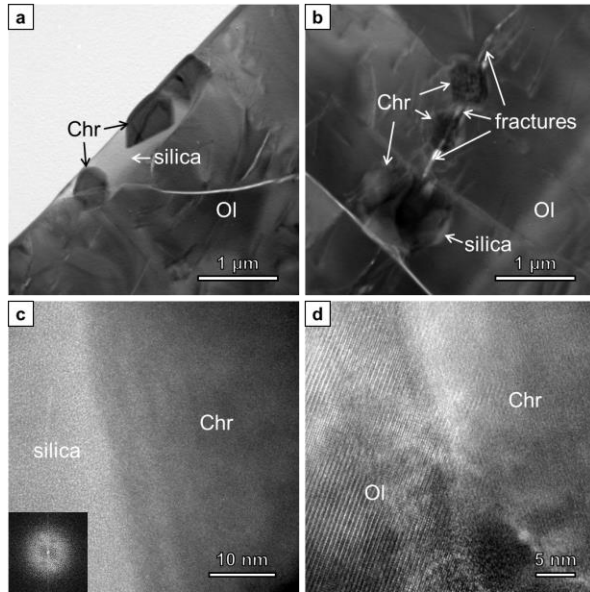


Fig. 3. BF-TEM (a-b) and HRTEM images (c-d) of the FIB section shown in Fig. 2. Amorphous silica partially encloses chromite or occurs as thin layers on chromite. No crystallographic orientation relationship is observed between chromite and olivine.

It is possible that the trails are crystallization products of trapped melts along rapid growth surfaces of olivine. Some incompatible and slow-diffusing elements, such as P and Al, often form oscillatory zoning in olivine due to solute trapping [e.g., 6]. Similarly, trapped melts in olivine were likely to be enriched in these elements. Since Cr and P concentrations in olivine are often positively correlated due to coupled substitution [e.g., 7], chromite may have also crystallized from the trapped melts. There are, however, some problems with this mechanism. First, the chromite + silica assemblage is unequilibrated with the olivine host. Although silica phases that may have formed by extensive crystallization have been reported in melt inclusions and mesostases of shergottites [e.g., 8-9], the mineralogy of these reported melts is distinct from that of the trails in this study. Second, this mechanism has difficulty explaining the linear shape of the trails that crosscut the P-zoning pattern, even if the olivine formed by skeletal growth [e.g., 10].

Alternatively, the trails are solid chromite grains and associated melts which were trapped along frac-

tures that have subsequently healed. The entrapment of solid chromite is consistent with the textural relationship between chromite and silica (e.g., partial enclosure). The trails are only present in the inner region of olivine and crosscut P zoning which may have been produced during magma ascent [6]; therefore, the entrapment of chromite and melts also occurred at this stage. However, such an evolved, silica-rich melt was unlikely to be present during the olivine crystallization.

From the discussion above, the formation of the chromite + silica trails requires interaction between olivine and trapped late-stage basaltic melts along fractures. This process can be expressed by the following reaction: $2\text{Fe}_2\text{SiO}_4_{[\text{Ol}]} + 2\text{Cr}^{2+}_2\text{SiO}_4_{[\text{Ol}]} + 4\text{Cr}_2\text{O}_3_{[\text{melt}]} + \text{O}_2_{[\text{melt}]} = 3\text{Cr}^{3+}_{4/3}\text{SiO}_4_{[\text{Ol}]} + 4\text{FeCr}^{3+}_2\text{O}_4_{[\text{Chr}]} + \text{SiO}_2_{[\text{silica}]}$. The Cr enrichment in the trapped melts was caused by solute trapping. The introduction of Cr^{3+} into olivine expelled Fe^{2+} from the structure due to vacancy substitution, resulting in an increase in Cr_2O_3 content and Mg# observed in the olivine in the trails. Chromium from both olivine and melts contributed to the formation of chromite. The preservation of silica may be attributed to rapid cooling during magma ascent. Amorphous silica has been reported in terrestrial olivines that have undergone oxidation at high temperatures [e.g., 11]. Diffusion and subsequent precipitation of chromite and silica should be easier to achieve in submicron-sized trapped melts, compared with larger melt inclusions, due to the limited diffusion distance.

Implications: The olivine-melt interaction mechanism implies that oxidizing agents were introduced during the late-stage crystallization of olivine megacrysts. This is consistent with the decrease in $\text{Cr}^{2+}/\text{Cr}^{\text{total}}$ in the rim of Y-98 olivine megacrysts [12] which implies a late-stage oxidation event, likely caused by degassing. Nonetheless, the absence of widespread micron-to-submicron chromite in Y-98, in contrast to chemically more enriched shergottites [e.g., 13], indicates that oxidation was significantly less intense in Y-98, possibly due to the limited degassing.

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