

A TEM STUDY OF THE SULFIDE REPLACEMENT ASSEMBLAGES IN LUNAR BRECCIA

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Introduction: Sulfide replacement textures present in Mg suite clasts of lunar breccia 67915 have been interpreted by numerous studies to have formed by the interaction of this lithology with a sulfur-bearing metasomatic fluid [1-4]. The sulfide replacement textures typically consist of secondary low-Ca pyroxene, troilite, oxide, and metallic Fe, pseudomorphically replacing primary igneous olivine (Figure 1a and 1b). The most prominent feature of the replacement textures is the presence of “myrmekite-like” intergrowths of low Ca-pyroxene and troilite. A cartoon depicting the relationship between

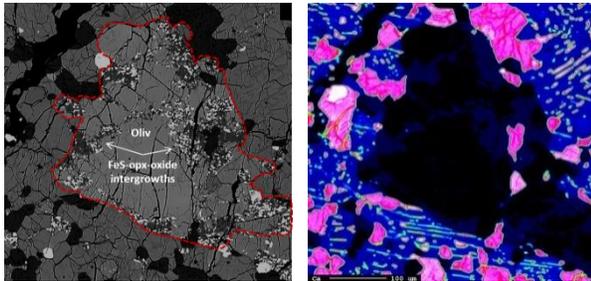


Figure 1. a. A macro-scale backscattered electron image (BSEI) of an olivine phenocryst that has been partially pseudomorphed by troilite-orthopyroxene-oxide intergrowths. The grain boundary of the olivine phenocryst is indicated with a red dashed line. b. A Ca K α x-ray map of the same area portrayed in the BSEI. In this image, distribution of the orthopyroxene intergrowths within the host olivine phenocrysts can clearly be distinguished. The field of view in each image is approximately 300 microns in width.

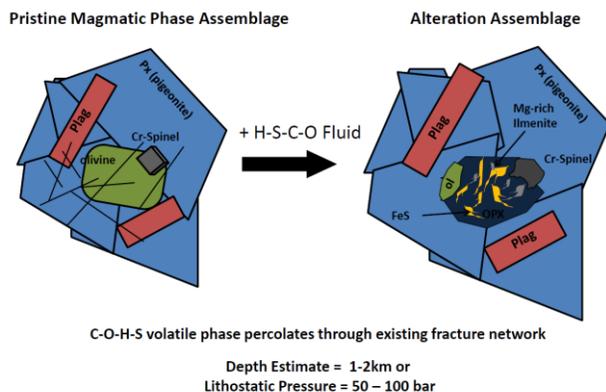


Figure 2. A cartoon of the fluid mineral-reaction responsible for the development of the sulfide replacement textures. The pressure and depth estimates have been taken from [3].

We have conducted a TEM investigation of the sulfide replacement assemblages for the purpose of gaining a better understanding of how the metasomatic phases grew at the expense of the existing mineral assemblage and fluid phase. Another equally important aim of this TEM study was to search for mineralogical evidence to further constrain the composition of the metasomatic fluid. In particular, the TEM work focused on determining whether or not the alteration assemblages also contained nanoscale graphite or chlorine-bearing phases.

TEM Methods Description: An FEI Quanta 3D Field Emission Gun FIB/SEM/EDS was used to image sample texture and chemistry at the nanoscale, select a specific nanoscale region, and cut and thin a micro-scale wide, nano-scale thick section for transmission electron microscope (TEM) analysis. The location of the FIB cut was selected because it traverses the entire alteration assemblage. A JEOL 2010 TEM with Oxford INCA system ultrathin window EDS (energy dispersive spectroscopy) detector was used for sample mapping of chemistry and selected area diffraction for phase analysis. A JEOL 2010F FASTEM field emission gun, capable of scanning transmission electron microscopy (STEM/TEM), with point to point resolution of 0.194 nm and minimum probe size of 0.14 nm was used for diffraction contrast and energy filtered TEM imaging. It is equipped with a Gatan GIF image filtering system for energy filtered TEM and electron energy loss spectroscopy (EELS), and an Oxford INCA system with ultrathin window EDS detector for nanoscale chemical analysis of light to heavy elements.

Results: Figure 3 contains a bright field image of the FIB cut, superimposed with electron diffraction patterns that were obtained for each phase. Our TEM imaging and analysis of the FIB section did not reveal the presence of any additional phases. Neither graphite nor Cl-bearing phases were identified in this TEM mount. For example, no Cl as an individual phase or in amorphous phases has been identified in area of the image in in Figure 3. However, the nano-scale observations of the reaction textures in the section did reveal some new details about

the kinetics of the sulfide replacement reactions. The electron diffraction patterns indicate that the orthopyroxene varies in its degree of crystallinity, ranging from amorphous, to a nanoscale polycrystalline aggregate, to a well-

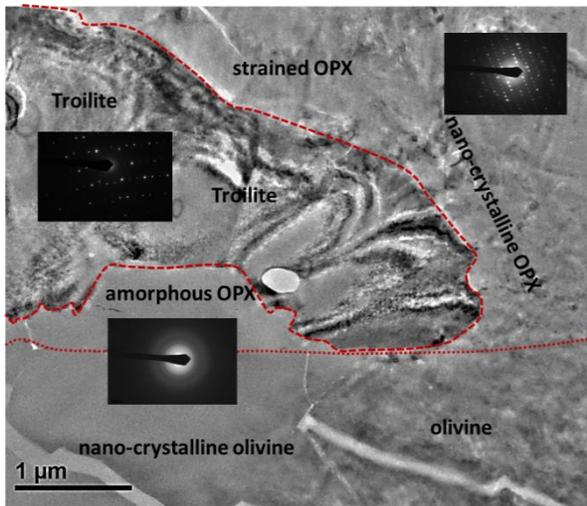


Figure 3. A bright field TEM image of the the sulfide replacement assemblage that was obtained on a FIB section. The dashed lines indicate the boundaries between different phases. The image is also superimposed with the electron diffraction patterns that were obtained for each of the phases identified by EDS. Olivine and orthopyroxene have been labeled with additional modifiers describing the degree of crystalline organization observed for each the phases.

developed single crystal of orthopyroxene in some regions (see Figure 3). The observed differences in the crystallinity of the reaction products suggest that the FIB cut has revealed snapshots of the alteration reactions in various states of structural organization and completion during the replacement reactions:



Figure 4 contains a high resolution bright field TEM image of the boundary between nano-crystalline orthopyroxene and replacement triolite. This illustrates the difference between the completely crystalline triolite and the nano-crystalline orthopyroxene. Another curious feature of the alteration assemblages is the occurrence of “stacking” faults in the triolite that are immediately adjacent to the most crystallographically “organized” orthopyroxene.

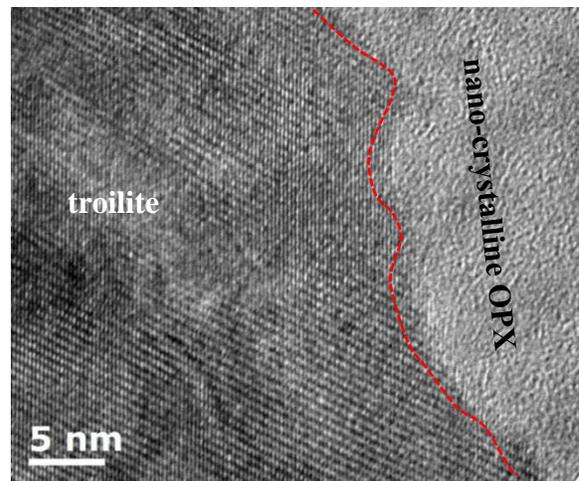


Figure 4. A high resolution bright field TEM image of the the sulfide replacement assemblage of the boundary between nano-crystalline orthopyroxene and triolite.

One possible explanation for these features is that the stacking faults develop along “mature” phase boundaries in order to help accommodate the volume change associated with sulfidation reactions.

Conclusions: The TEM investigation of the sulfide replacement textures has brought forth interesting new observations about the crystalline state of the sulfidation reaction products. Additionally, this work did not uncover any nanoscale graphite or Cl bearing phases in the sulfidation assemblages. While this result does not preclude the presence of either Cl or C in the metasomatic fluid phase believed to be responsible for the formation of the sulfidation assemblages, it does place important constraints on the possible activity of graphite in the system. Confining the activity of graphite to values less than one has important implications for the composition of the fluid phase. Recent modeling efforts have shown that the abundance of carbon bearing species (primarily CH_4) in the fluid phase is limited for graphite undersaturated lunar volatiles.

References: [1] Haskin and Warren (1991) Lunar Source Book, 357-474 [2] Norman et al. (1995) GCA, 59, 831-847 [3] Shearer et al. (2012) GCA, 83,138-158 [4] Bell et al. (2015) LPSC abstract