

INDIGENOUS CARBON-RICH MATTER ASSOCIATED WITH UNUSUAL SECONDARY DEPOSITS IN NAKHLA: A COMPLEX FORMATION AND PRESERVATION HISTORY. K. L. Thomas-Keprta¹, S. J. Clemett¹, N. Baskar², Z. Rahman¹, E. K. Gibson³, S. J. Wentworth¹, D. S. McKay³; ¹Jacobs JETS, NASA/JSC, Houston, TX 77058 (kathie.thomas-keprta-1@nasa.gov); ²Texas A&M University, College Station, TX 77840; ³ARES, NASA/JSC, Houston, TX 77058; ³Deceased, formerly ARES, NASA/JSC, Houston, TX 77058.

We report the identification of aqueous altered assemblages on interior fracture surfaces of the Martian meteorite Nakhla concomitant with indigenous C-rich matter. The alteration assemblages are of demonstrably Martian origin and are consistent with formation from low temperature, CO₂-rich, aqueous brines with variable compositions. They appear as μm-thick layers adhering to and overlying the silicate groundmass. Carbonaceous (C-rich) matter is found, in multiple cases, to be embedded within these aqueously altered assemblages. In one instance, the secondary mineralogy is consistent with iddingsite, while in the other cases the absence of phyllosilicates indicates a complex heterogeneous alteration environment. The latter supports a recently proposed reaction mechanism for silicate weathering which proceeds through a coupled interfacial dissolution-precipitation mechanism [1]. It is not yet clear whether the encapsulated C-rich phases present within these alteration coatings were actively involved in, and/or were a product of, the aqueous alteration process or were simply passively sequestered. However, in the former case it is difficult to reconcile with the contemporary hypothesis proposed by [2] of electrochemical reduction of CO₂ by spinel-group minerals, sulfides in a brine electrolyte. We suggest it would be wise to eschew any single hypotheses.

Methods: The Nakhla samples used in this work were acquired from the British Museum of Natural History. Chips from Nakhla were fractured under clean conditions using stainless steel tools. Fragments revealing fresh interior fracture surfaces were selected and documented prior to sputter-coating with Pt (~1 nm) and characterized using field emission scanning electron microscopy (FESEM) and energy dispersive X-ray spectroscopy (EDX). Regions of interest (ROIs) were subsequently extracted by focused ion beam (FIB) microscopy and thinned to electron transparency for characterization by field emission scanning transmission electron microscopy (FESTEM) and EDX.

Results: *Figures 1-3* shows three regions, in separate Nakhla samples, of secondary alteration assemblages with encapsulated C-rich matter. In *Fig. 1, Area 1*, C-rich ROIs (arrows) are surrounded by a cluster of salt crystals, partially embedded in an underlying layer of iddingsite surrounded by a second, texturally smooth, iddingsite region. Such layering with differing textures has been reported previously [e.g., 3]. The salt crystals are predominantly NaCl with occasional MgCl₂, and CaSO₄ that appears infrequently partly intergrown with

the NaCl. A FIB section through the bowl-shaped feature (red box) and the underlying iddingsite, analyzed by TEM/EDX point spectra and mapping, reveals the feature is primarily C-rich containing O with lesser amounts of Si, S, Ca, Cl, F, Na, and minor Mn & Fe. In addition a small N peak is apparent. While the F_{Kα1} peak is commonly obscured by the Fe_{Lα} peak, the extremely small Fe_{Kα} peak eliminates this overlap problem and indicates the C-rich phase contains a significant amount of F. *Fig. 2, Area 2* shows a C-rich feature, which appears as a thin layer ~15 × 20 μm in size, from which a FIB section was extracted. STEM/EDX spectra show the C-rich ROI contains N, O, Si, Ca & S. The right side of the ROI contains Na & K while the left side is enriched in Mn. EDX spectra indicate N is present at significant amounts. *Fig. 3, Area 3* shows multiple layers with the uppermost being amorphous and rich in Si. The underlying layer is fayalite and lined with a thin (~50 nm thick) alteration rim. A thin layer of amorphous, C-bearing material, containing major Mg with Cl & detectable K, lies between the Si-rich and fayalite layers.

Discussion: The absence of phyllosilicates in two of the three alteration surfaces, thus differentiating them from iddingsite, indicates that aqueous alteration within Nakhla proceeded through a spatially heterogeneous and temporally evolving chemical and physical environment. We find evidence to support the coupled dissolution-precipitation mechanism for silicate alteration, described in detail by [4, 5]. In this model, altered mineral surfaces are characterized by a distinct surface layer that is amorphous, less dense, and enriched in silica compared to the host mineral. The C-rich matter which is intimately associated with a variety of mineral alteration assemblages in Nakhla, displays unusual diverse range of compositions; some contain N and/or F with divalent cations including Mg, Si & Mn. We suggest it has likely been both formed *and* preserved by the interplay of multiple processes; any single process being inadequate to describe the complex nature of Martian organic matter.

References: [1] Thomas-Keprta *et al.* (2018) 49th LPSC Abst. # 2781. [2] Steele *et al.* (2018) *Sci. Adv.* 4: eaat5118. [3] McKay D.S. *et al.* (2009) *Proc. SPIE* doi:10.1117/12.832317. [4] Hellmann *et al.* (2013) *Procedia Earth & Planet. Sci.* 7: 346-349. [5] Hellmann *et al.* (2015) *Nature Materials*. DOI 10.101038/NMAT4172.

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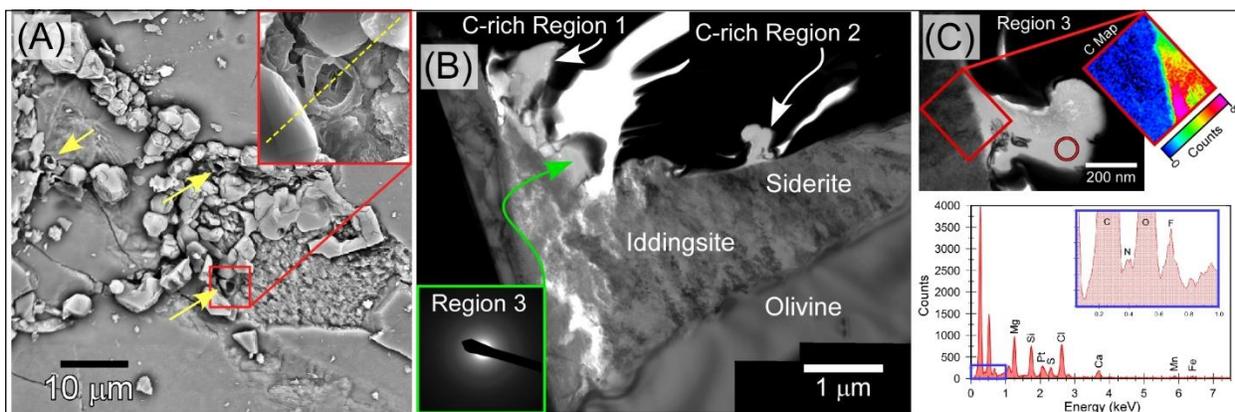


Figure 1: (A) SEM view (Area 1) of freshly fractured Nakhla surface. Salt crystals and C-rich features (yellow arrows) lie embedded within iddingsite layers. Inset (red box) expanded view of C-rich feature; yellow dashed line marks position of extracted FIB section. (B) TEM view of FIB section with three C-rich regions noted. (C) Upper, high magnification TEM view of Region 3 with C element map inset. Lower, EDX spectrum of region denoted by the red circle with inset showing C, N, O & F peaks.

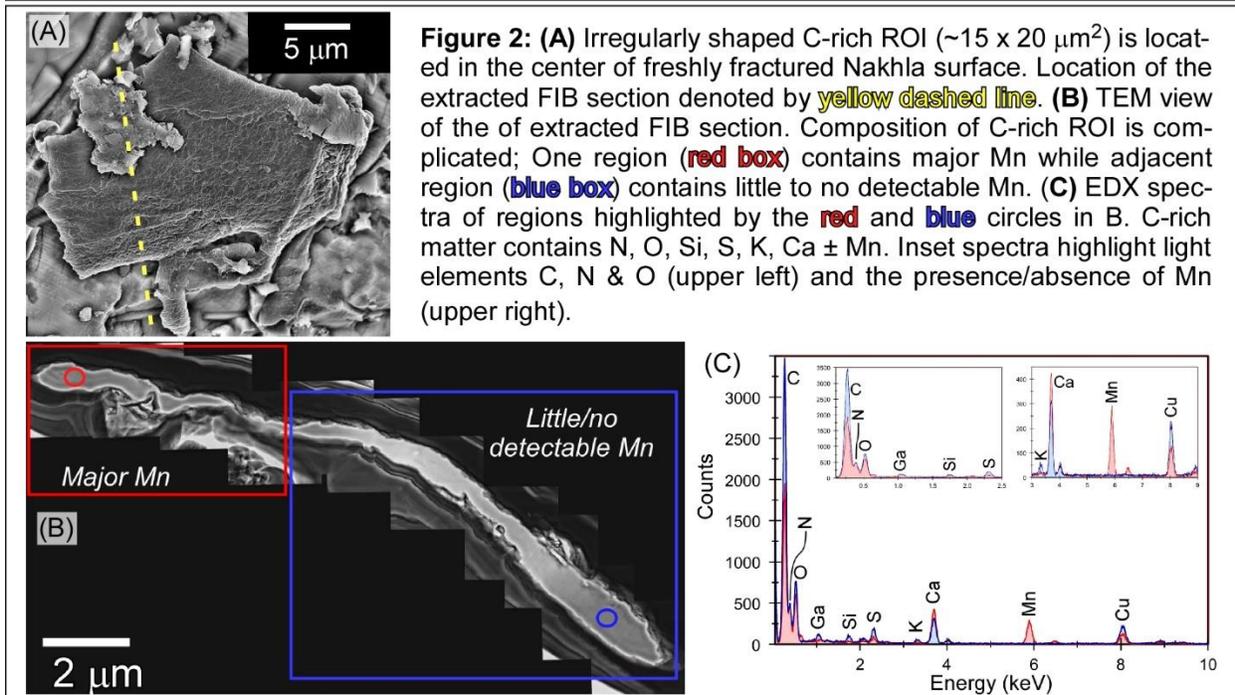


Figure 2: (A) Irregularly shaped C-rich ROI (~15 x 20 μm²) is located in the center of freshly fractured Nakhla surface. Location of the extracted FIB section denoted by yellow dashed line. (B) TEM view of the of extracted FIB section. Composition of C-rich ROI is complicated; One region (red box) contains major Mn while adjacent region (blue box) contains little to no detectable Mn. (C) EDX spectra of regions highlighted by the red and blue circles in B. C-rich matter contains N, O, Si, S, K, Ca ± Mn. Inset spectra highlight light elements C, N & O (upper left) and the presence/absence of Mn (upper right).

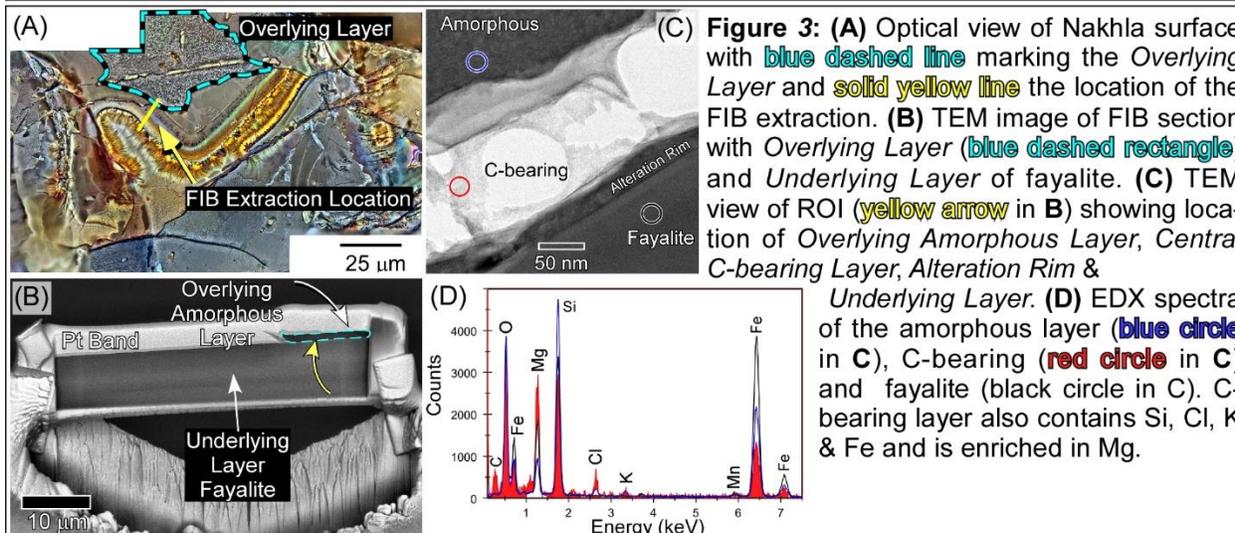


Figure 3: (A) Optical view of Nakhla surface with blue dashed line marking the Overlying Layer and solid yellow line the location of the FIB extraction. (B) TEM image of FIB section with Overlying Layer (blue dashed rectangle) and Underlying Layer of fayalite. (C) TEM view of ROI (yellow arrow in B) showing location of Overlying Amorphous Layer, Central C-bearing Layer, Alteration Rim & Underlying Layer. (D) EDX spectra of the amorphous layer (blue circle in C), C-bearing (red circle in C) and fayalite (black circle in C). C-bearing layer also contains Si, Cl, K & Fe and is enriched in Mg.