XPS, SEM, AND MICRO-RAMAN INVESTIGATIONS OF TAGISH LAKE (C2-UNG) METEORITE FUSION CRUST.

X. Shehaj[1,2], S. Caporali[3,4], B. Cortigiani[4,5], M. Ricci[5], G. Giuli[6], E. Palomba[2], G. Pratesi[1,2], [1]Dipartimento di Scienze della Terra, Università degli Studi di Firenze, Via G. La Pira 4, 50121 Firenze, Italy xhonatan.shehaj@unifi.it, [2] INAF-IAPS, Istituto di Astrofisica e Planetologia Spaziali, Via Fosso del Cavaliere 100, 00133 Roma, Italy, [3] Dipartimento di Ingegneria Industriale, Università degli Studi di Firenze, Via di S. Marta 3, 50139 Firenze, Italy, [4]Unità di ricerca Interdipartimentali – Material CHaracterization LAB (MATCHLAB) – Università degli Studi di Firenze, [5]Dipartimento di Chimica, Università degli Studi di Firenze "Ugo Shiff", Via della Lastruccia 3, 50019, Sesto Fiorentino, Firenze, Italy, [6]Università di Camerino, Scuola di Scienze e Tecnologie, sez. Geologia, Via Gentile III da Varano, I-62032, Camerino, Italy

Introduction: Fusion crust is a thin (few millimetres) dark layer which cover the surface of all fresh-fall meteorites, and form by vigorous interactions with the Earth atmosphere during their entry [1]. However, remains still controversial the redox state during fusion crust formation [2]. In order to better understand these chemical processes, in this work, we present a chemical and mineralogical surface study of Tagish Lake (C2-Ung) meteorite fusion crust.

Methods: Surface chemical analysis was performed by X-ray Photoelectron Spectroscopy (XPS) in an PREVAC standard PSE system equipped with non-monochromatic X-ray source – Al Kα – model RS 40B1. The pressure during the experiment was keep below 10^{-9} mbar.

Scanning Electron Microscope (SEM) analyses were performed using a Zeiss EVO MA15 model. An accelerating voltage of 15-kV and beam current of 10-nA were employed to collect backscattered electron (BSE) images and energy-dispersive X-ray spectroscopy (EDS) analyses.

Raman spectra were obtained by using a Renishaw RM2000 Raman microscope. The 514 nm laser radiation, from an argon ion laser was used. Laser power on the sample was adjusted between 0.01 and 0.5 mW, to avoid over-heating of the sample.

For these investigations, a fusion crust grain (~ 5 mm in size) of Tagish Lake meteorite was mounted - without any chemical-physical treatment - in omicron standard flag-type sample holder using a special Platinum basket. Moreover, in order to minimize the effects induced by atmospheric contamination, the grain was sputtered by Ar^+ (1 keV) for 20 min before starting the XPS measurements. Subsequent to the surface analysis, a little portion (~ 2 mm) of the same fusion crust sample was broken and embedded as polished mount (in cross-section), with the aim to characterize its interior structure by SEM analysis.

Results and discussion: The surface of the fusion crust shows an irregular topography with lobe-shaped protrusions ridges bordered by subspherical cavities (Fig. 1). The surface is covered by a thin plaquette Fe-oxides layer characterized by mosaic texture (Fig. 1,2). SEM cross-section investigation shows that the external portion of the fusion crust surface is make up by a thin Fe-oxides layer (~ 5 μm), mainly composed by magnetite, although zoned olivine (Fe-rich rim), glassy mesostasis, rounded Ni-rich, and relict chromites grains were also detected (e.g., Fig. 1-2). Moreover, no evidence of terrestrial contaminants have been found in the fusion crust surface.

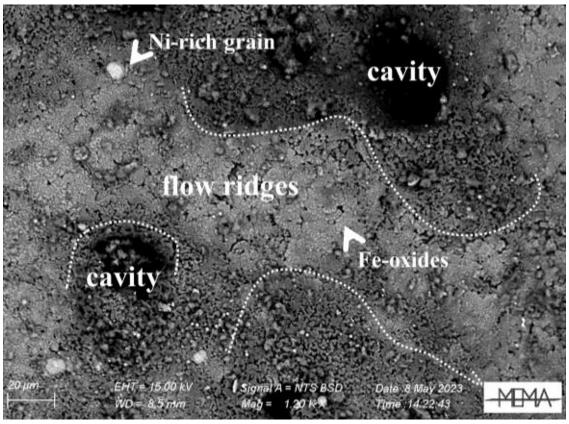

Fig. 1 SEM-BSE image of the surface of Tagish Lake fusion crust showing an irregular topography with lobe-shaped protrusions flow-ridges and subspherical cavities. A thin Fe-oxides layer (high brightness) covers the surface of fusion crust, mainly composed by magnetite and accessory wüstite grains.

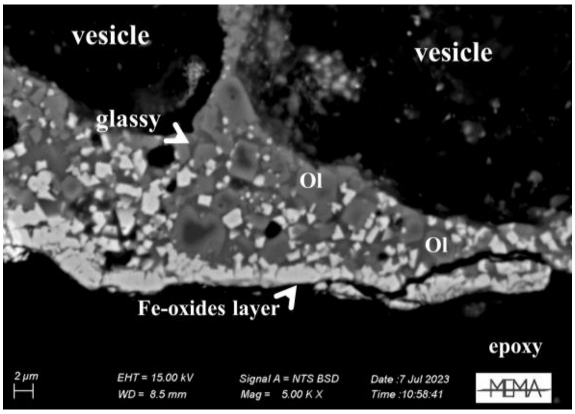

Fig. 2 SEM-BSE image of the cross section of Tagish Lake fusion crust. Typical texture and mineralogy of the external portion, composed by a thin (few μm) layer of Fe-oxides in outer most part,zoned olivine (Ol) phenocrystals, and glassy mesostasis.

However, graphite and wüstite grains were detected by micro-Raman analysis (e.g., 3). Moreover, observed bands exhibited greater width, indicating the presence of amorphous or less ordered material, and / or of chemically heterogeneous glass.

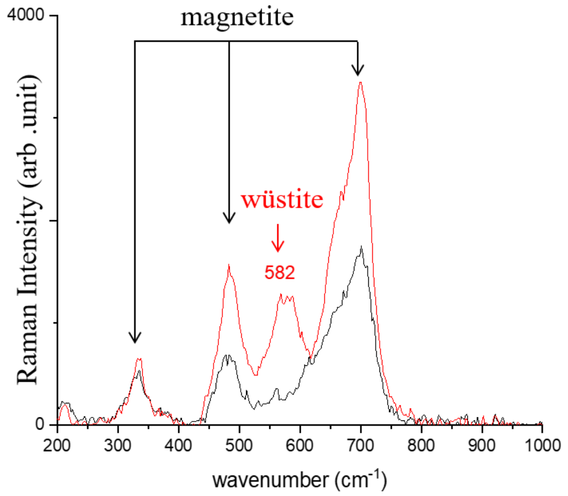

Fig. 3 Raman spectra, collected in two different points on the fusion crust surface of Tagish Lake meteorite, show peaks identified as wüstite (peak located at ~ 580–590 cm^{-1}) and magnetite.

As far as the XPS analysis, S-2p, C-1s, Si-2p, O-1s, and Fe-2p photoelectron peaks were acquired for fusion crust elemental determination, and calibrated by 2p silicon transition in silicates (102.6 eV). Photoelectron binding energies provide quantitative and chemical information (e.g. valence states) for the outermost ~ 5-10 nm of sample surfaces.Therefore, they are useful to investigate the outermost Fe-oxides layer in Tagish Lake fusion crust. Considering that the Fe2p spectrum includes both the Fe2p3/2 and the Fe2p1/2 spin-orbit coupling features, spectra were deconvoluted into Fe2p3/2 and Fe2p1/2 peaks utilizing spectral fitting parameters provided by [3]. As a result, 23% of the iron was identified as Fe(III) in oxides, 41% of the Fe(II) was associated with iron oxides, and 36% of the Fe(II) with silicate material (Fig. 4).

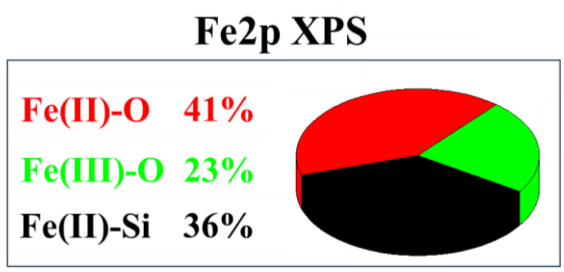

Fig. 4 relative abundance of iron species obtained from Fe 2p XPS spectra.

Sulfur 2p and Carbon 1s XPS spectra exhibit a high depletion in the surface of the fusion crust.

For the first time we report a detailed surface chemical and mineralogical characterization of the Tagish Lake fusion crust. XPS, SEM, and micro-Raman analysis show that fusion crust is dominated by a thin (few µm) Fe-oxides surface layer, and depleted in volatile elements (e.g., C, S). However, the presence of wüstite and graphite grains identified by micro-Raman analysis suggest that Tagish Lake meteorite fusion crust may have experienced a surface (few µm) reduction during its entry into the Earth's atmosphere, probably promote by the pyrolysis of carbonaceous materials, as also suggested by [1].

Acknowledgement: The authors wish to thank "Centro di Servizi di Microscopia Elettronica e MicroAnalisi" (MEMA) and "Laboratory of Molecular Magnetism" (LaMM) at the Università degli Studi di Firenze (Italy) for analysis and sample preparation. The research was funded by the ASI-INAF Project "Attività scientifiche per l'estensione della missione Hayabusa 2"

References: [1] Genge M. and Grady M. (1999) *Meteoritics & Planet. Sci.*, *34, 341*-356. [2] Pittarello L. et al. (2019) *Meteoritics & Planet. Sci* 54 (7) 1563–1578. [3] Biesinger M., et al. (2011) *App. Surf. Sci.* 257, 2717-2730.