

**PRIMITIVE OXYGEN-, NITROGEN-, AND ORGANIC-RICH VEIN PRESERVED IN A XENOLITH HOSTED IN THE METAMORPHOSED CARANCAS METEORITE.** Q. H. S. Chan<sup>1</sup>, M. E. Zolensky<sup>2</sup>, Y. Kebukawa<sup>3</sup>, I. Franchi<sup>1</sup>, I. Wright<sup>1</sup>, X. Zhao<sup>1</sup>, Z. Rahman<sup>4</sup> and J. Utas<sup>5</sup>, <sup>1</sup>Planetary and Space Sciences, School of Physical Sciences, The Open University, Walton Hall, Milton Keynes MK7 6AA, UK ([Queenie.Chan@open.ac.uk](mailto:Queenie.Chan@open.ac.uk)), <sup>2</sup>ARES, NASA Johnson Space Center, Houston, TX 77058, USA, <sup>3</sup>Faculty of Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogayaku, Yokohama 240-8501, Japan, <sup>4</sup>Jacobs, NASA Johnson Space Center, Houston, TX 77058, USA, <sup>5</sup>Institute of Geophysics and Planetary Physics, UCLA, Los Angeles, California, USA.

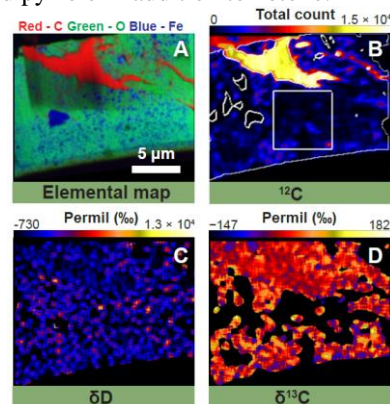
**Introduction:** Primitive xenolithic CI-like carbonaceous (C) clasts are sometimes hosted within meteorites of a different origin (ordinary chondrite, ureilite, howardite, and eucrite) [e.g., 1, 2]. These xenoliths contain aggregates of macromolecular carbon (MMC), which are often present as discrete grains and exhibit a wide range of structural order and chemical compositions [1]. The Carancas meteorite is a H4-5 that impacted south of Lake Titicaca, Peru in 2007. While the meteorite exhibits extensive recrystallization of the matrix indicating metamorphism [3], it contains dark, CI-like clasts that show no evidence of heating. Similar to other xenolithic clasts, the examined C clast of Carancas contains MMC, which however exists in the form of a vein-like structure dissimilar to the typical occurrence of MMC in meteorites. We investigated the organic and isotopic compositions of the organic-rich vein with C,N,O-X-ray absorption near-edge structure (XANES), Raman spectroscopy, and NanoSIMS, in order to constrain its possible origin.

**Samples and Analytical Techniques:** Two ~100 nm-thick focused ion beam (FIB) sections (Carancas 1 with the C-rich vein, and Carancas 2) were subsampled from a selected Carancas C clast using a Quanta 3d field-emission gun FIB instrument at NASA JSC. The FIB sections were analysed with C,N,O-XANES microspectroscopy using the scanning transmission X-ray microscopes (STXM) at BL4U of UVSOR, Institute for Molecular Science. The sections were then studied with a Jobin-Yvon Horiba LabRAM HR (800 mm) Raman microprobe at The Open University (OU) using a 514.53-nm (green) laser for which the power was maintained at ~60  $\mu$ W. The Raman C parameters (*param.*) – the peak position ( $\omega$ ) and full width half-maximum ( $\Gamma$ ) of each Raman band – were determined by simultaneous peak fitting to the two-peak Lorentzian and Breit–Wigner-Fano model [4] and linear baseline correction. The H,C,N,O isotopic compositions of the ~15 nm Au-coated FIB sections were analysed by isotopic imaging with a NanoSIMS 50L ion microprobe at OU with a primary Cs+ beam of ~1.5–3.5 pA.

### Results and Discussion:

**C,N,O-XANES.** The STXM elemental map outlines the ~10  $\mu$ m C-rich vein (red area) in the Carancas 1 section (Figure 1A). The C-XANES spectrum of the C-

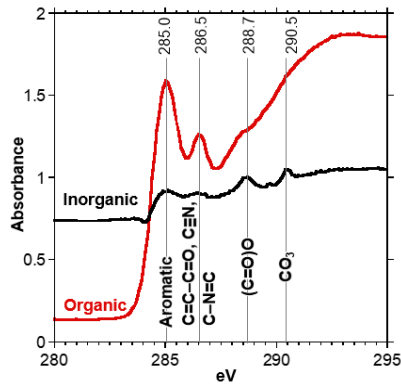
rich vein (Figure 2) shows two major absorption features: (1) 285.0 eV: alkenyl and aromatic (C=C) carbon, and (2) 286.5 eV: ketone (C=O), nitrile (C $\equiv$ N), and/or pyrrole and imidazole [5]. A weak 288.7 eV peak was observed which corresponds to carboxyl carbon (O–C=O). The notable feature at 286.5 eV is also consistent with the strong C=O feature (~531.0 eV) in the O-XANES spectrum. The presence of ketones suggests the onset of aqueous alteration on the parent body [6]. The N-XANES spectrum shows adsorption features around 398.6 and 399.7 eV (imine [C=N], nitrile [C $\equiv$ N], pyridine) and 401.1 eV (amide, pyrrole [C–NHx]) [5], which are consistent with the 286.5 peak identified in the C-XANES spectrum as potentially nitrile and pyrrole in addition to ketone.



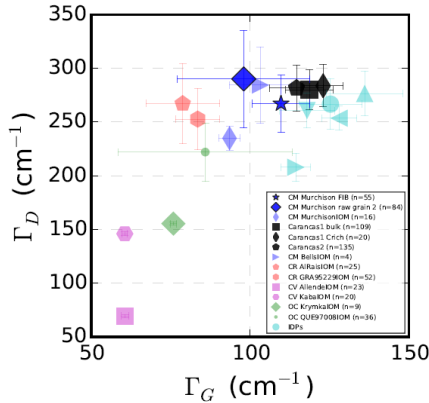
**Figure 1.** (A) STXM elemental map of Carancas 1. (B) NanoSIMS <sup>12</sup>C elemental map, and isotopic images of (C)  $\delta$ D and (D)  $\delta^{13}$ C.

The C-rich vein is unique in its organic chemistry. It is atypical of primitive chondritic insoluble organic matter (IOM) (e.g. Murchison), as the 286.5 eV feature is less prominent and the 288.7 eV feature is more pronounced in the latter (Figure 2). Thus, the C-rich vein has a higher ketone but lower carboxyl content, which indicates that aqueous alteration occurred on the parent body but the process was not severe, as carboxylic acid would have been formed via further oxidation of ketone. The C=O feature of the vein in the O-XANES spectrum is prominent and comparable to the OM in interplanetary dust particles (IDPs), but the carboxyl content is significantly lower in the vein.

**Raman spectroscopy.** The most typical Raman peaks of carbonaceous materials are the first-order defect (D) band at  $\sim 1360\text{ cm}^{-1}$  and the graphite (G) band at  $\sim 1580\text{ cm}^{-1}$  [7]. Changes in the *param.* of the OM in C chondrites correspond to the nature of the organic precursors and the structural order of the aromatic units [e.g., 8]. We compared the *param.* of the organics hosted within the C-rich vein and the matrix of the Carancas meteorite to the IOM of chondritic meteorites. Carancas OM shows an affinity to the primitive (unheated) CM chondrites (Figure 3). The OM in the C-rich vein is more primitive than its matrix and its *param.* are comparable to IDPs. We have also studied a raw grain, IOM and a FIB section prepared from Murchison matrix, and found that the *param.* are not influenced by the sample form, thus allowing direct comparison between the FIB section of the Carancas meteorite to the meteoritic IOM.



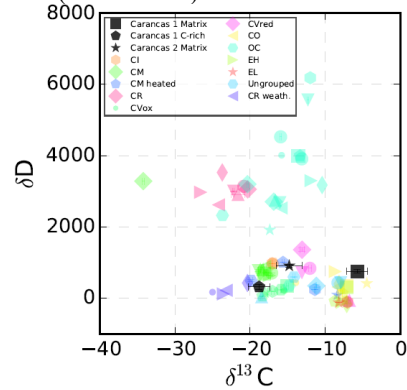
**Figure 2.** C-XANES spectra of the C-rich vein (organic) and the matrix (inorganic) of the Carancas 1 FIB section.



**Figure 3.** The  $\Gamma_D$  and  $\Gamma_G$  of the Carancas sample compared to that of the IOM of meteoritic organics and IDPs [9].

**NanoSIMS analysis.** We used the isotopic compositions of the Carancas sample to interpret the origin of its OM. NanoSIMS isotopic images are shown in Figure 1 (C,D), and the C vs. H isotopic compositions are plotted in Figure 4. In general, the C, H isotopic compositions of the Carancas C clast sample are different from that of ordinary chondrites (which typically have

higher  $\delta D$  values,  $>2000\text{‰}$ ) but show an affinity to CMs/CIs. The C-rich vein is depleted in  $^{13}\text{C}$  ( $\delta^{13}\text{C} = -19 \pm 1\text{‰}$ ) and D ( $\delta D = +316 \pm 73\text{‰}$ ) compared to the C clast matrix ( $\delta^{13}\text{C} = -6 \pm 1\text{‰}$ ;  $\delta D = +754 \pm 52\text{‰}$ ) (Figure 4). Carancas 2 does not contain a similar C-rich vein and probably better represents the meteorite bulk. The C,H isotopic values of Carancas 2 ( $\delta^{13}\text{C} = -15 \pm 11\text{‰}$ ;  $\delta D = +911 \pm 41\text{‰}$ ) are comparable to that of CIs. The lower  $\delta D$  enrichments in CIIIs compared to the CR2s ( $\delta D \sim 3000\text{‰}$ ) indicates the exchange of D-poor water during aqueous alteration [10, 11]. The  $\delta^{15}\text{N}$  value of the C-rich vein ( $-31 \pm 16\text{‰}$ ) is slightly higher than that of the matrix ( $-100 \pm 4\text{‰}$ ).



**Figure 4.** The C vs. H isotopic composition of the Carancas samples compared to meteorite IOM [10].

**Conclusion:** The studied Carancas meteorite C clast is unheated primitive C1 material that was incorporated into the D-type parent body subsequent to the latter's thermal event. The varied isotopic compositions of the C-rich vein and the C clast bulk suggest that they were processed under different aqueous conditions but the water is D-poor in both events, or the C-rich vein was produced in a later, shorter aqueous event that sequestered organics from the surroundings and resulted in further isotopic fractionation. The association of the C-rich vein with parent body aqueous alteration likely accounts for its vein-like structure. The XANES features of the C-rich vein in Carancas suggest that it originates from a parent body that is enriched in O- and N-bearing compounds.

**References:** [1] Chan Q.H.S. *et al.* (2018) *Science Advances*, 4, eaao3521. [2] Kebukawa Y. *et al.* (2017) *GCA*, 196, 74-101. [3] Connolly H.C. *et al.* (2008) *MAPS*, 43, 571-632. [4] Ferrari A.C. and Robertson J. (2000) *Physical Review B*, 61, 14095-14107. [5] Cody G.D. *et al.* (2008) *MAPS*, 43, 353-365. [6] Sephton M.A. (2002) *NPR*, 19, 292-311. [7] Tuinstra F. and Koenig J.L. (1970) *JCM*, 4, 492-499. [8] Busemann H. *et al.* (2007) *MAPS*, 42, 1387-1416. [9] Chan Q. *et al.* (2017) *MetSoc*, 6157. [10] Alexander C.M.O.D. *et al.* (2007) *GCA*, 71, 4380-4403. [11] Alexander C.M.O.D. *et al.* (2012) *Science*, 337, 721-723.