

INTERACTION BETWEEN PHYLLOSILICATES AND ORGANIC NANOGLOBULES IN RYUGU. L. Daly^{1,2,3}, M. R. Lee¹, P. A. Bland⁴, W. Smith⁵, S. McFadzean⁵, P-E. Martin¹, P.A.J. Bagot³, D. Fougerouse⁴, D.W. Saxey⁴, S. Reddy⁴, W.D.A. Rickard⁴, T. Noguchi^{7,8}, H. Yurimoto⁹, T. Nakamura¹⁰, H. Yabuta¹¹, H. Naraoka¹², R. Okazaki¹², K. Sakamoto⁹, S. Tachibana¹³, S., Watanabe¹⁴, Y. Tsuda¹⁵, K. Burgess¹⁶, R. Stroud¹⁶ and the Min-Pet Fine Sub-team. ¹School of Geographical and Earth Sciences, University of Glasgow, Glasgow, UK. (luke.daly@glasgow.ac.uk). ²Australian Centre for Microscopy and Microanalysis, The University of Sydney, Sydney, NSW, Australia, ³Department of Materials, University of Oxford, Oxford, UK. ⁴Space Science and Technology Centre, School of Earth and Planetary Sciences, Curtin University, Perth, WA, Australia. ⁵Materials and Condensed Matter Physics, School of Physics and Astronomy, University of Glasgow, Glasgow, UK. ⁶Geoscience Atom Probe Facility, John de Laeter Centre, Curtin University, Perth, WA, Australia. ⁷Division of Earth and Planetary Sciences, Kyoto University; Kitashirakawaoiwake-cho, Sakyo-ku, Kyoto 606-8502, Japan. ⁸Faculty of Arts and Science, Kyushu University; 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan. ⁹Department of Earth and Planetary Sciences, Hokkaido University; Kita-10 Nishi-8, Kita-ku, Sapporo 060-0810, Japan. ¹⁰Department of Earth Science, Graduate School of Science, Tohoku University; 6-3 Aoba, Aramaki, Aoba-ku, Sendai 980-8578, Japan. ¹¹Earth and Planetary Systems Science Program, Hiroshima University; 1-3-1 Kagamiyama, Higashi-Hiroshima City, Hiroshima, 739-8526, Japan. ¹²Department of Earth and Planetary Sciences, Kyushu University; 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan. ¹³UTokyo Organization for Planetary and Space Science, University of Tokyo; 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan. ¹⁴Department of Earth and Environmental Sciences, Nagoya University; Furo-cho, Chikusa-ku, Nagoya 464-8601, Japan. ¹⁵Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency; 3-1-1 Yoshinodai, Chuo-ku, Sagami-hara, Kanagawa 252-5210, Japan. ¹⁶US Naval Research Laboratory, Washington, DC, USA

Introduction: In December 2020 the Hayabusa2 mission delivered 5.4 g of material from the C-type asteroid 162173 Ryugu for laboratory analysis on Earth [1]. Preliminary characterization of these returned materials indicate that Ryugu is most like the highly altered CI chondrite meteorites [1]. These meteorites are rich in water and organic materials and are good candidates for the late delivery of water, organics and volatiles to the early Earth during the final stages of its accretion, making them important samples for understanding how Earth became a habitable world [2,3]. However, all carbonaceous chondrite meteorites have been contaminated by Earth's environment, with organic molecules being particularly susceptible to terrestrial alteration [2]. As such, understanding the nature of organic compounds within Ryugu grains that have not been exposed to the terrestrial atmosphere is crucial to understanding the original organic make up of C-type asteroids and by extension the molecules that were delivered to the early Earth [4-6].

The majority of the organic material in carbonaceous chondrite meteorites is in the form of macromolecular, acid-insoluble organic matter (IOM), including discrete particles identified as nanoglobules [2]. Some nanoglobules have anomalous D and N compositions that are suggestive of an origin in a radiation-rich environment, either the interstellar medium or outer Solar System [2,7]. Here we report the occurrence and structure of organic nanoglobules within grains from the regolith of Ryugu.

Methods: A Ryugu grain was mounted on Cu tape using a micromanipulator. The grain's surface was

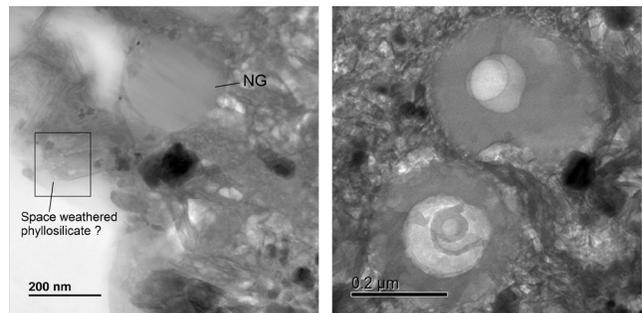


Figure 1. Bright-field TEM images of organic nanoglobules in Ryugu: a rounded solid nanoglobule in a TEM wafer analyzed at NRL (left) and two rounded nanoglobules that have a double walled concentric shell-like structure analysed at the UofG (right).

imaged using a Zeiss Sigma scanning electron microscope (SEM) at the University of Glasgow (UofG) at 2 kV. The grain was sputter coated with Cr to protect its outer surface. APT samples and electron transparent wafers for transmission electron microscopy (TEM) were extracted from regions of interest identified by SEM using a Ga-focused ion beam (FIB) microscope at the UofG following established protocols [8,9]. These samples contained magnetite, carbonate and matrix. High angle annular dark-field (HAADF) images and electron energy loss spectroscopy (EELS) maps were collected using a JEOL ARM200F field-emission scanning TEM operated at 200 kV. APT samples were analysed on the LEAP 5000 at the University of Oxford. A TEM sample from another Ryugu grain was prepared by JAXA and was analyzed at Naval Research Laboratory (NRL).

It is important to note that at no stage was this Ryugu grain or the TEM wafers exposed to a carbon source. It was not mounted in resin or coated with carbon and so any organic materials within the sample should be indigenous to Ryugu.

Results: TEM investigations revealed a cluster of three organic nanoglobules within a $\sim 15 \times 15 \mu\text{m}$ TEM wafer that are enclosed within the phyllosilicate-rich matrix (Fig. 1). These nanoglobules had a double walled concentric ring structure comprising 4-6 layers (Fig. 1). The outer surfaces of the nanoglobules are not smooth and contain phyllosilicate crystals that are growing into their surfaces (Fig. 1). EELS mapping reveals that each layer within the organic nanoglobule has a variable amount of carbon, with the outer layers containing higher carbon and oxygen abundances than the interior (Fig. 2). Nitrogen was also detected within one layer of a nanoglobule (Fig. 2). Similar solid nanoglobules have been observed in a TEM wafer of another Ryugu grain characterized at NRL (Fig. 1) [4-6].

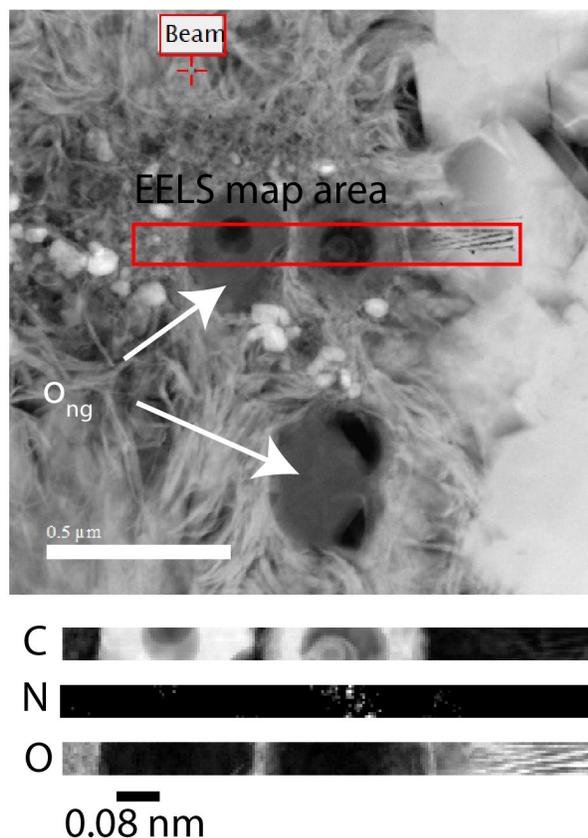


Figure 2. HAADF image (upper) and EELS maps (lower) of organic nanoglobules (O_{ng}) within Ryugu. EELS reveals heterogeneities in carbon and oxygen abundance as well as the presence of nitrogen within one of the inner layers.

TEM characterization of magnetite within the Ryugu grain shows that in most cases these minerals contain abundant inclusions. APT of one such grain has identified an inclusion that is carbon-rich (Fig. 3) and further characterization and interpretation of this inclusion will be presented at the meeting.

Discussion: The nanoglobules observed here are similar in shape and structure to other double walled nanoglobules characterized previously in CMs, CIs and comet 81P/Wild 2 [2,7] and Ryugu [4-6]. The complex layers and radial variation in chemistry suggests multiple phases of formation/sequential alteration events. The ingrowth of matrix phyllosilicates into the outer surfaces of the nanoglobules is likely to be due to the intense aqueous alteration experienced by Ryugu materials [1]. These reactions results in the progressive alteration of organic molecules, which is typical of carbonaceous chondrites that have experienced high degrees of aqueous alteration [10].

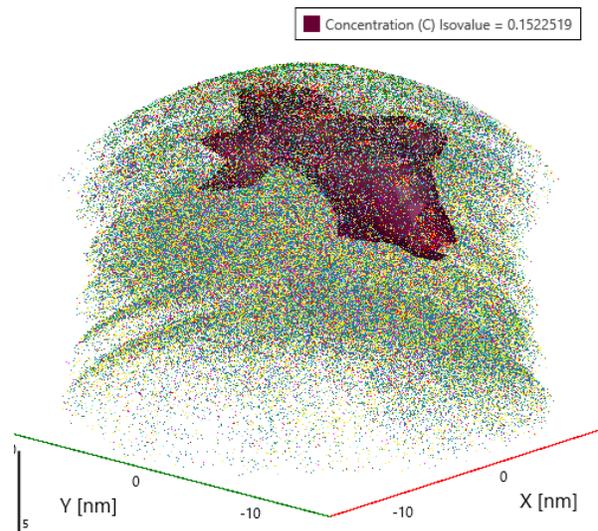


Figure 3. APT dataset of a magnetite grain from Ryugu that has a carbon-rich inclusion.

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