CNHOS contents with their isotopic compositions and preliminary organic profiles from the Hayabusa2 samples

Yoshinori Takano[1], Hiroshi Naraoka[2], Nanako O. Ogawa[1], Yasuhiro Oba[3], Toshiki Koga[1], Toshihiro Yoshimura[1], Saburo Sakai[1], Naohiko Ohkouchi[1], Hisayoshi Yurimoto[3], Tomoki Nakamura[4], Takaaki Noguchi[5], Ryuji Okazaki[2], Hikaru Yabuta[6], Kanako Sakamoto[7], Shogo Tachibana[7,8], Sei-ichiro Watanabe[9], Yuichi Tsuda[7] and the Hayabusa2-initial-analysis SOM team

[1] JAMSTEC, [2] Kyushu Univ., [3] Hokkaido Univ., [4] Tohoku Univ., [5] Kyoto Univ., [6] Hiroshima Univ., [7] JAXA, [8] Univ. Tokyo, [9] Nagoya Univ.

The successful collection and recovery of the Ryugu sample [1,2] are leading us to a valuable opportunity for revealing the properties of the carbonaceous asteroid in the Solar System history; -What is Ryugu? -What are the origins and characteristics of light elements (C, N, H, O, and S)? -What do their isotopic compositions tell us? -How do they record the primordial chemical evolution on the asteroid? -How did the interaction of water, organic matter, and minerals affect the evolution and diversity of indigenous molecules? To answer those important issues by using state-of-the-art small-scale analysis, the SOM (Soluble Organic Matter) team have been firstly focusing on (i) the initial bulk profiles, especially for the elemental abundance of carbon (C), nitrogen (N), hydrogen (H), oxygen (O), sulfur (S) with the isotopic compositions of δ^{13}C, δ^{15}N, δD, δ^{18}O and δ^{34}S, respectively, and (ii) the molecular profiles to understand more deeply for nature of indigenous SOM [3-5]. For instance, if endogenous water-mineral interactions occurred in the asteroid, some aqueous alteration signatures (e.g., process relevant products including carbonates and other precipitates) should have been recorded to the pristine sample in the bulk and molecular levels. Assuming the interactions above mentioned, we can trace the potential *in-situ* temperature of the alteration process by using clumped isotope surveys of minerals [6]. To assess the objectives, we have been conducting rehearsal analyses for analytical optimizations and sequential sample processes [3-5, e.g., Figure 1], with a scope of solid and soluble organic aspects [6-9]. In order to deal with samples of unknown identity, especially for bulk nitrogen scale, we validated the dynamic range of δ^{15}N profiles covered on the basis of pioneering works and compilations for the Inner and Outer Solar System [e.g., 10].

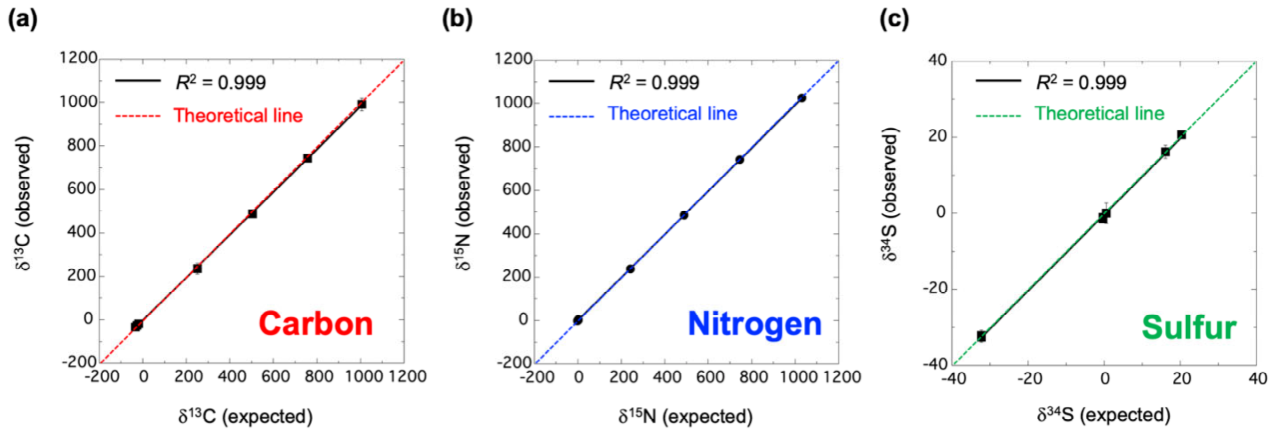

Figure 1 The high precision and high accuracy analytical optimization using reference standards of carbon (C), nitrogen (N), and sulfur (S) for covering wide range isotopic compositions: **(a)** δ^{13}C, ‰ vs. VPDB; within ^{13}C-enriched and ^{13}C-depleted profiles, **(b)** δ^{15}N, ‰ vs. Air; within ^{15}N-enriched and ^{15}N-depleted profiles, **(c)** δ^{34}S, ‰ vs. VCDT; within ^{34}S-enriched and ^{34}S-depleted profiles. The x-axis and y-axis stand for the nominal value (= expected) and the measured value (= observed), respectively. Prior to the Hayabusa2 samples, those analytical validations using the nano-EA/IRMS system [3,4,7] were performed during the rehearsal analyses (e.g., several carbonaceous chondrite of CM2 and C2-ungrouped: unpublished data) at JAMSTEC. We have confirmed that there was no memory effect in the analytical lines due to sequential process. For further of optimization ultra-small-scale sulfur (S) quantification with δ^{34}S validation, please see the latest update [11].

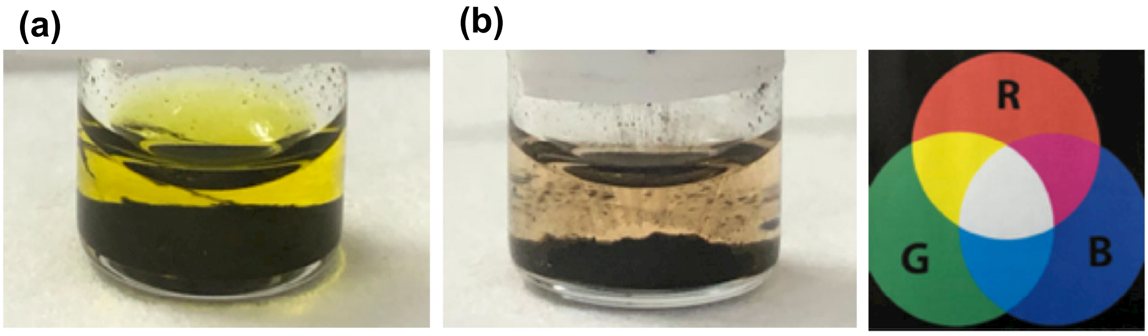

Figure 2 (a, b) Capturing the representative colors during the sequential solvent extraction and the wet chemical treatment for the Hayabusa2 samples (Ryugu, sample ID: A106 & C107). After solid-liquid separation, the colored supernatant with yellowish and pinkish colors were observed in both A106 and C107, the photo taken in the cleanroom at Dept. Earth Planet Sci., Kyushu Univ. Since dissolved inorganic elements and organic-inorganic complex molecules also have some kind of chromaticity depending on the affinity of the solvent, we are in the process of conducting detailed verification. Please see also the residue of insoluble organic matter (IOM, black color) on the bottom of the vial. The onsite RGB color scale is shown.

We observed some of the colored supernatant during the sequential solvent extraction processes of Ryugu sample (Figure 2). These extraction samples have been safely distributed to the SOM team members and are being analyzed in detail at their laboratories [12]. The residue of IOM fraction has been also seamlessly transported to the other initial analysis team for further description [13]. Here, we note that the colors of the extract show the chemical responses of the extractable indigenous organic molecules to the inherent affinity of the solvent from low to high polarity (i.e., dependent on hydrophilicity, hydrophobicity, and amphiphilicity with both properties). Also, the colored supernatant may indicate that there is a certain amount of components with a significant absorption spectrum (e.g., chemically various carbon skeleton with N-, S-, O-hetero structures). Regarding the molecular-level analysis, we are currently in the process of combining the pieces of the raw data profiles [12], and we expect synergistic discussions at this symposium in terms of native organic properties within the history of the Ryugu.

References

[1] Tachibana S. et al., #1289, 52nd LPSC (2021); Tachibana S. et al., *Geochem. J.* 48, 571-587 (2014).
[2] Yada T. et al., #2008, 52nd LPSC (2021).
[3] Naraoka H., Takano Y., Dworkin, J. P. et al., #6314, 82nd Met Soc (2019); Naraoka H. et al., #1362, 51st LPSC (2020).
[4] Ogawa N. O. et al., 51st LPSC (2020); Ogawa N. O. et al. *Earth, Life, Isotopes*, Kyoto Univ. Press. (2010).
[5] Yoshimura T. et al., #1971, 51st LPSC (2020); Yoshimura, T. et al. *J. Chromatogr. A* 1531, 157-162 (2018).
[6] Wang Z. et al., *Anal. Chem.* 92, 2034-2042 (2019); Bonifacie M. et al., *Geochim. Cosmochim. Acta* 200, 255-279 (2017).
[7] Kebukawa Y. et al., *Meteorit Planet Sci.* 56, 1311-1327 (2021); Kebukawa Y. et al., *Geochim. Cosmochim. Acta* 271, 61-77 (2020); Chan H. S., et al., *Earth, Planets Space*, 68, 7 (2016).
[8] Oba Y. et al., *Nature Commun.* 10, 4413 (2019); Oba Y. et al., *Nature Commun.* 11, 6243 (2020).
[9] Takano Y. et al., *Inter. J. Mass Spectrom.* 462, 116529 (2021).
[10] Kerridge J.F. *Geochim. Cosmochim. Acta* 49, 1707-1714 (1985); Füri, E. and Marty B., *Nature Geosci.* 8, 515-522 (2015).
[11] Ogawa N. O. et al., #PR0203, Geochem. Soc. Jpn. (2021).
[12] Naraoka H., Takano Y., Dworkin, J. P., this symposium. & the other reports from the Hayabusa2-initial-analysis SOM team.
[13] Initial reports from the Hayabusa2-chemistry, -stone, -sand, -volatile, -IOM team at this symposium.