

**RYUGU PARTICLES CONTAIN SULFUR IN MULTIPLE OXIDATION STATES.** M. Bose<sup>1</sup> and R. A. Root<sup>2</sup>,  
<sup>1</sup>School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287, USA, <sup>2</sup>Department of Soil, Water & Environmental Science, University of Arizona, Tucson, Arizona 85721, USA. (Maitrayee.Bose@asu.edu)

**Introduction:** Of all the extraterrestrial materials found on Earth, particles from asteroids Itokawa and Ryugu are the least terrestrially contaminated. Ryugu rocks contain ubiquitous phyllosilicate minerals [1, 2], have never experienced temperatures above 300°C [2], and are more porous than meteorites [3,4]. Asteroid Ryugu is similar to CI (Ivuna-like) carbonaceous chondrite (CC) meteorites [1].

The sulfur-bearing organic matter in Ryugu is currently unknown and is the subject of this study. Sulfur functional group chemistry of extracted insoluble organic matter (IOM) from CCs is rich and includes sulfides and oxidized organic sulfur [5–8]. There is some variability of sulfur speciation among the different meteorite groups with the CIs containing sulfates, heterocyclic sulfur, and aliphatic sulfur [e.g., 6]. On the other hand, CCs like the CV CC Allende contain primarily disulfide and elemental sulfur, with no organosulfurs [5]. Experimental work has shown that hydrothermally treated IOM exhibit transformations in their oxidation states of sulfur and can produce thiophene compounds [5]. The results indicate that secondary alteration processes can be responsible for the redox cycling of sulfur and subsequent production of organosulfurs but the conditions facilitating the chemical production and possible reaction pathways of organosulfurs in meteorites remain unknown. The particles brought back from Ryugu will allow us to investigate the chemical evolution of sulfur in a low-temperature, water-rich asteroid body. Here, we present results from the analysis of sulfur oxidation states in two Ryugu particles from chamber A.

**Ryugu Samples:** Two particles AA0070 (2 mg; 2281  $\mu\text{m}$ ) and AA0093 (1.6 mg; 1999  $\mu\text{m}$ ) were mounted in an anaerobic chamber purged with H<sub>2</sub> and N<sub>2</sub>. Particle AA0070 fragmented during manipulation and produced finer material so we produced 2 sets of samples from this particle. The larger fragment was glued onto polyimide tape (Kapton). The finer set of particles from AA0070 were dispersed onto the tape but were subsequently exposed to air to allow comparison to the samples produced under an O<sub>2</sub>-free environment. The second particle AA0093 was pressed onto a pre-made 99.9% pure indium pellet mount, and polished with 1 and 10  $\mu\text{m}$  diamond films. Both samples were transferred from the anaerobic chamber in a nitrogen purged container and analyzed under a He atmosphere.

**Methods:** Speciation of the Ryugu particles were investigated with synchrotron X-ray absorption near edge structure (XANES) spectroscopy at beam line 14–3, at the Stanford Synchrotron Radiation Lightsource (SSRL), a National Laboratory user facility operated by

the Department of Energy (DOE). The X-ray beam was operated at 3 GeV and 500 mA, and a double-crystal monochromator (Si [111] crystal,  $\phi = 90$ ) was used to tune the incident energy on the sample. A Kirkpatrick-Baez (KB) mirror system was used to achieve a micro-focused beam. Energy was calibrated using the centroid of the first peak of sodium thiosulfate, assigned to 2472.02 eV. Energy resolution ( $\Delta E/E$ ) at the sulfur edge is  $10^{-4}$ . Several coarse-scale X-Ray fluorescence maps ( $500 \times 500 \mu\text{m}^2$ ) of both Ryugu particles were initially obtained. This enabled us to create the sulfur heat maps to find sulfur-rich hotspots, and its association with other elements such as Al, Si, and P. Subsequently finer-scale investigations both at the 3 and 1 micron-scale resolutions were conducted. Whenever possible, XANES spectra were acquired at the 3  $\mu\text{m}^2$  spot sizes to confirm the nature of the sulfur-bearing domain.

Before we measured the samples, we tested the adhesive (Gorilla Super Glue™), Kapton tape and the indium used for mounting the particles, and all were sulfur-free.

**Results and Discussion:** We scanned a total of 15 and 8 areas in particle AA0070 and AA0093, respectively. The total sulfur (<2500 eV) abundance in the Ryugu particles is higher compared to that reported in Murchison and GRA 95229 [5,8]. The spectra acquired from the fine-grained particles exposed to oxygen indicate presence of sulfates and organosulfurs, albeit small in magnitude. Similarly, both Ryugu particles contain sulfate, specifically Na-sulfate.

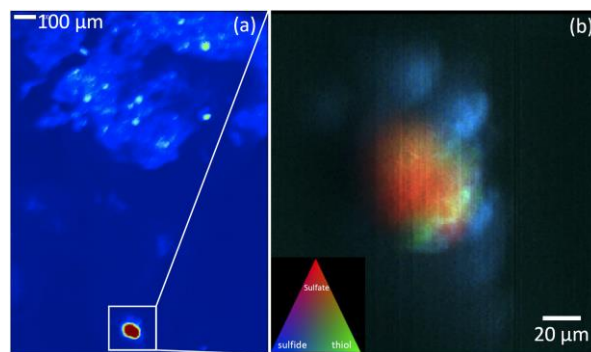


Figure 1. (a) A sulfur heat map acquired on particle AA0070 showing sulfur-bearing domains. (b) An organosulfur coating (shown in green) around a sulfate grain in the Ryugu particle AA0070.

Most of the sulfides are of mixed composition based on the double peaks observed in the spectra. Several areas in both particles are a fine-grained mix of different Fe-, Ni- and other metal-bearing sulfides. It would

require suitable standards for further assessment of their relative abundances.

A large area ( $\sim 75 \text{ } \mu\text{m}^2$ ) in particle AA0070 contains a  $40 \text{ } \mu\text{m}^2$  sulfate grain (2482.5 eV), with a partial coating of thiol (2473.2 eV) and is surrounded by abundant sulfides ( $< 2472 \text{ eV}$ ) (Fig. 1). Thiols are the simplest of the sulfur-bearing organic compounds containing the  $-\text{SH}$  functional group. The organosulfur coating shown in green (Fig. 1) shows a clear signature of thiols, likely a thiosulfate, owing to the presence of a sulfate peak in the XANES spectra. A second organosulfur-bearing grain was found in particle AA0093, which is also thiol-rich in nature (Fig. 2) and has a peak corresponding to the methionine sulfoxide. In this case, it does not have a corresponding sulfate peak (Fig. 2).

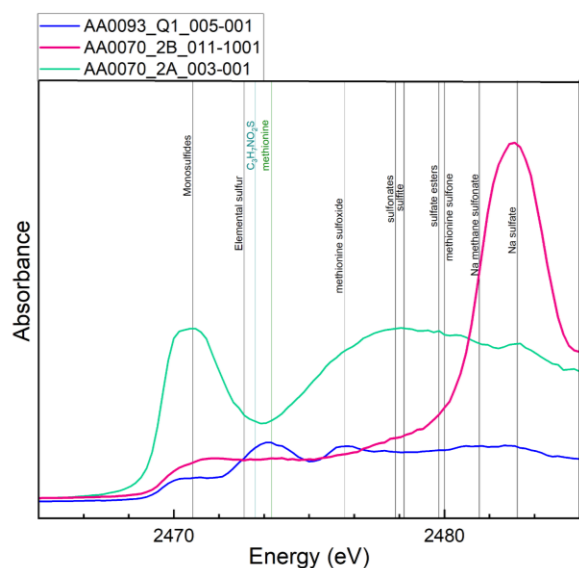


Figure 2. Typical spectra from Ryugu particles AA0070 and AA0093.

Thiol peaks have been observed in CR CC GRA 95229 [8]. In addition, the occurrence and overlap of the elemental sulfur peak in the spectra can make the assessment of thiol contents difficult. However, that is not the case with our observations in the Ryugu particles. The occurrence and abundance of thiols in both Ryugu particles shows clearly that these phases are likely destroyed in meteorites quite promptly after fall or during sample processing to extract IOM.

We show here that formation of organic sulfur compounds in a low temperature asteroidal environment is inevitable, and perhaps an essential part of meteoritic chemistry. Sulfur itself is ubiquitous in meteorites and in Ryugu (this work; [9]), and present in sulfur-bearing minerals (such as pyrrhotite, pentlandite) that can produce  $\text{H}_2\text{S}$ . These sulfur-bearing mineral assemblages can act as either redox buffers, surface catalysts or both. Additionally, synthesis of thiols from abiotic precursors

requires carbon sources such as  $\text{CO}_2$  and  $\text{CO}$  as the most likely starting materials. These starting materials namely  $\text{H}_2\text{S}$  and  $\text{CO}_2/\text{CO}$  can lead to the formation of methanethiol, ethanethiol and other longer-chained thiols. Such reactions to produce thiols occur readily in hydrothermal vents on Earth [e.g., 10]. At lower temperatures, reaction kinetics may be overcome by the availability of additional catalytic compounds [11]. We will utilize a combination of thermodynamic calculations and geochemical modeling to identify the conditions where thiol compounds may be thermodynamically favorable and stable in aqueous reactions and (2) investigate the possible reactions and formation mechanisms responsible for generating thiols in low-temperature asteroidal environments.

**Conclusions:** Sulfurization of  $\text{O}_2$ -poor organic matter in Ryugu may be a key process occurring in Ryugu's interior. It reduces reactive functional groups and adds cross links between small unstable molecules and likely converts them into recalcitrant organosulfur coatings on minerals.

**References:** [1] Kitazato K. et al. (2019) *Science*, 364, 272–275. [2] Kitazato K. et al. (2021) *Nature Astronomy*, 5, 246–250. [3] Okada T. et al. (2020) *Nature*, 579, 518–522. [4] Grott M. et al. (2019) *Nature Astronomy*, 3, 971–976. [5] Bose M., Root R. A., and Pizzarello S. (2017) *MAPS*, 52, 546–559. [6] Orthous-Daunay F.-R. et al. (2010) *EPSL*, 300, 321–328. [7] Copper G. W. et al. (1997) *Science*, 277, 1072–1074. [8] Bose M. and Root R. (2018) *Lunar & Planetary Science* 49, Abstract #2098. [9] Nakamura T. (2022) *Science*, DOI: 10.1126/science.abn86. [10] Schulte M. D. and Rogers K. L. (2004) *GCA*, 68, 1087–1097. [11] Cody G. D. et al. (2000) *Science*, 289, 1337–1340.