Origin and preservation of organosulfurs and sulfates in Ryugu

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We report identification of various organosulfur molecules and a large sulfate grain with a coating of methionine (CH₃-SH) in situ in two Ryugu particles A0070 and A0093 using synchrotron micro-X-ray fluorescence imaging and micro-X-ray absorption near edge structure spectroscopy. Subsequently, we measured the oxygen, carbon, nitrogen and sulfur isotopes in the sulfate grain with the methionine coating with nano-scale secondary ion mass spectrometry (NanoSIMS). The methionine coating on the sulfate grain is isotopically anomalous ($\delta^{15}N = +62 \pm 2$ %). The sulfate grain shows oxygen isotope ratios ($\delta^{17}O = -11.0 \pm 4.3 \%$), $\delta^{18}O = -7.8 \pm 2.3$ ‰) that are akin to the anhydrous, ¹⁶O-poor chondrule-like olivine and pyroxene grains in Ryugu but has sulfur exhibiting mass-independent isotopic fractionation (δ^{33} S = $-0.1\pm 1.6\%, \ \delta^{34}S = +9.8 \pm 0.9 \ \%, \ \Delta^{33}S = +5 \pm 2 \ \%).$ Thermodynamic calculations show that the sulfate and methionine can simultaneously form during aqueous alteration within Ryugu's parent body, under reduced conditions (pH $> \sim$ 7) and low temperature, in the presence of N-rich organic molecules. Although constraints from previous literature set an upper limit to the temperature of < 150°C of the Ryugu parent body [e.g., K. McCain, et al. Nature Astronomy 7, 309-317 (2023)], sulfur chemistry indicates that the temperature experienced by some Ryugu particles could not have exceeded ~90 °C. In addition, the mass-independent fractionation of sulfur is attributed to isotopically selective photodissociation of H₂S vapor in warm (T > 70 K) molecular gas, which produces isotopically heavy (Δ^{33} S > 0 ‰) elemental sulfur S⁰ that is accreted into ices, ultimately accreted by the Ryugu parent body. This work extends the heliocentric zone where isotopically anomalous sulfur is found and strengthens the case for inheritance of molecular cloud material.