Can SIMS measurements constrain the D/H ratio of water on Ryugu?

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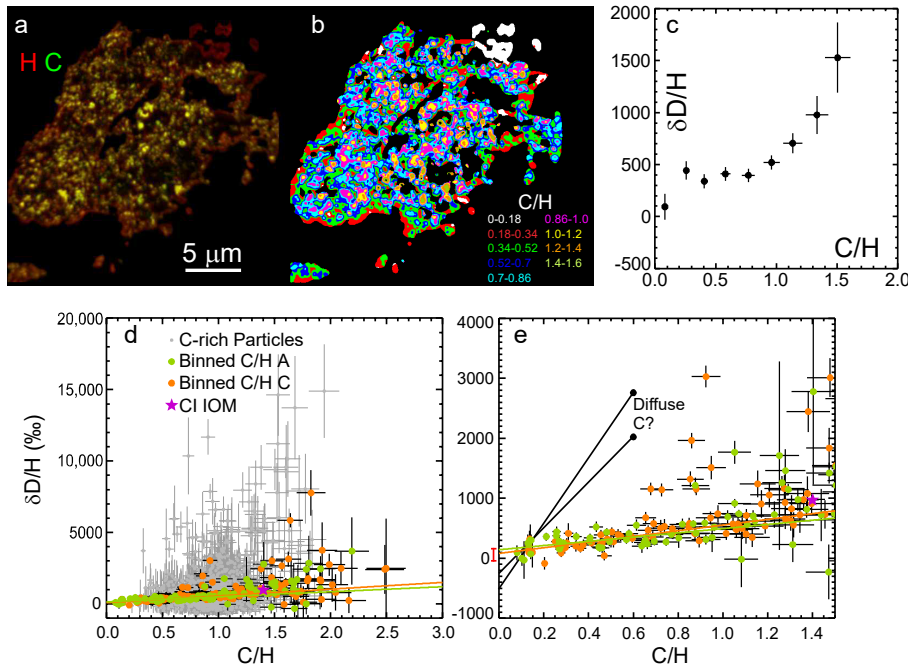[2]*School of Earth and Space Exploration, Arizona State University, USA*
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We have previously reported the use of the Cameca NanoSIMS ion microprobe to characterize H, C, and N isotopes on a sub-micrometer scale in particles returned by the Hayabusa2 spacecraft from C-asteroid Ryugu [1, 2]. These data show that macromolecular organic-rich particles in Ryugu samples are remarkably isotopically heterogeneous on μm scales with compositional distributions similar to those of carbonaceous chondrites (CCs), including CIs, the closest meteorite analog to Ryugu [3]. Recently, Piani et al. [4] have used large-geometry SIMS (Cameca ims-1280) data to conclude that Ryugu water has δD/H = +74 ± 117 ‰. Since the NanoSIMS has much higher spatial resolution than the ims-1280, we have re-examined our data to investigate whether they can provide additional information on Ryugu's water composition. Our results agree well with those of [4], but we argue below that it is not possible with current ion probe data sets to infer the H_2O D/H composition on Ryugu with any degree of confidence.

Prior work on CCs and Ryugu samples [4-6] has assumed that ~10-μm-scale SIMS H-isotope measurements represent two-component mixtures between water of hydration (with C/H=0) and organic matter (with higher C/H), based on observed correlations between measured C/H and D/H ratios. Extrapolation of fitted linear trends to the data to C/H=0 then yields the inferred D/H of the intrinsic H_2O. Shown as grey circles in Fig. 1d are the C/H ratios and δD values we have previously found in organic-rich particles, typically a few 100 nm in diameter, based on 20 fragments of Ryugu particles A0108-13 (12 fragments) and C0109-2 (8 fragments) pressed into Au foils. The instrumental mass fractionation and C/H calibration were corrected based on a terrestrial organic standard. The large scatter in these data precludes linear extrapolation. We thus chose to bin the imaging data by defining regions-of-interest (ROIs) in each image whose C/H ratios spanned specific intervals (e.g., Figs. 1a-c). The C/H and D/H ratios are generally correlated within an image (e.g., Fig. 1c) but the variable presence of anomalously D-rich or D-poor grains (hot/coldspots) often leads to non-linear trends. Nevertheless, when the data are combined for all 20 particles, clear linear trends are observed below C/H~1 for both the Chamber A and Chamber C grains (green and orange symbols in Fig. 1d-e). Outliers are due to the presence of D hotspots or coldspots. The solid green and orange lines indicate linear fits to the data below C/H=1 (excluding outliers). The fit lines intersect the Y-axis at δD=142 ‰ and 82 ‰, respectively, in excellent agreement with the results of [4] (red error bar), acquired with a different instrument on different samples.

The linear trends seen in Fig. 1d,e support the idea that, when averaged over relatively large areas, the data represent two-component mixing. At the high C/H end, the endmember is clearly the average of the ubiquitous C-rich particles present throughout the Ryugu samples, i.e., the grey symbols in Fig. 1d. We note that insoluble organic matter (IOM) extracted from CI chondrites [magenta star; 7] lies close to but slightly above the Ryugu trend lines. This supports previous measurements indicating that Ryugu IOM has lower D/H than IOM from CIs [8] but could also reflect a possible mis-calibration of the C/H ratios from measured C/H secondary ion signals in the NanoSIMS. The identification of the low C/H endmember is more ambiguous. Transmission electron microscopy and synchrotron-based transmission x-ray microscopy studies have shown that in Ryugu samples the phyllosilicates are intimately mixed with a "diffuse" organic material [9-11]. This diffuse C ("dC") is spectroscopically distinct from the larger particulate organic grains, for example showing a CO_3 feature (not associated with carbonate minerals) and often showing a higher abundance of aliphatic compounds [11]. The intimate association of the dC with the clay minerals means that even at the highest NanoSIMS spatial resolution, one cannot distinguish H coming from the dC and that coming from the water. Thus, the trend in fact represents *3-component* mixing where the low C/H endmember is itself a mixture of H_2O and dC. Since the two forms of organics (dC and particles) are spectrally distinct, they also could

have distinct C/H and D/H ratios on average. For example, the black lines on Fig 1e indicate mixing between water with δD= -200 or -500 ‰ (as inferred for CI chondrites by [12]) and supposed diffuse C components arbitrarily assumed to have C/H~0.6 (based on assumed higher aliphatic content) and δD~2000 or 3000‰, respectively. Since these lines intersect with the low-C/H end of the Ryugu trends, the data are fully consistent with Ryugu water having a D/H much lower than inferred by [4], *if the dC indeed has higher D/H and/or lower C/H on average than the larger organic grains and the mixing ratio between dC and phyllosilicates is roughly constant on the scale of the measurements*. Without a way to independently determine the composition of the dC, we conclude that SIMS measurements like those used here and by [4-6] cannot unambiguously resolve the D/H of water in Ryugu samples. Moreover, dC has also been seen to be present in CI, CM, and CR chondrites [13], suggesting that previous SIMS D/H measurements of these should be revisited. Finally, we note that under O⁻ primary ion bombardment, the secondary ion yield of H⁺ is higher from hydrated silicates than from organics [14]. High-resolution NanoSIMS measurements of Ryugu samples with the Hyperion RF plasma O source, compared with Cs-based measurements of the same materials, may allow for better discrimination of the water endmember from the dC and provide a better estimate of the D/H of Ryugu water.

Figure 1. a) Color-coded NanoSIMS map of H and C in a Ryugu particle b) ROIs defined by pixels within selected C/H ratio bins. c) δD versus C/H for ROIs from panel b. d,e) δD versus C/H for 20 analyzed Ryugu fragments. Vertical red error bar is y-intercept reported by [4].

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