WATER IN ASTEROID RYUGU IS DEUTERIUM-RICH COMPARED TO EARTH AND CI CHONDRITES.

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Introduction: Large variations in the deuterium to hydrogen (D/H) ratio across the Solar System can be used to probe the origin and evolution of volatile elements in the solar nebula, including the source(s) of water and prebiotic molecules on Earth [1, 2]. JAXA's Hayabusa2 spacecraft returned 5.4 g of material from two sites on asteroid Ryugu to Earth in December 2020. Initial analyses of Ryugu samples revealed strong chemical and mineralogical similarities to Ivuna-type (CI) carbonaceous chondrite (CC) meteorites [3]. It has been suggested that Ryugu's parent body (and CIs) originated from much farther out in the protoplanetary disk than other CCs [4].

The Ryugu regolith grains are dominated by phyllosilicate minerals, carbonates, magnetite, and sulfides indicating extensive aqueous alteration on Ryugu's parent body in the first few million years of Solar System evolution. The Ryugu samples thus offer the possibility of determining the D/H ratio of asteroidal water with much less concern about terrestrial contamination than for meteorites that may have interacted with Earth's environment for decades or more. However, the ubiquitous presence of (generally D-rich) macromolecular organic matter (OM) finely interspersed with silicates and other phases in CCs makes direct determination of water D/H ratios difficult. Alexander et al. [1] used measurements of D/H and C/H ratios of bulk meteorites and extracted OM residues to estimate chondrite water compositions. More recently, Piani et al. [2, 5] have used secondary ion mass spectrometry (SIMS) analyses with a Cs^+ beam to measure C/H and D/H ratios on ~10-μm scales. Linear fits to the data allow extrapolation to C/H=0 to estimate the D/H of the water end-member, although scatter in the data due to μm-scale heterogeneity in the composition of OM leads to relatively large errors. Application of this method to Ryugu samples [6] has indicated a water δD value of +59±121 ‰ (2σ) that overlaps within errors that of CI Orgueil measured by the same method.

It has been long recognized that SIMS analysis of H as H^+ secondary ions under O^- bombardment strongly favors hydrated silicate minerals over organic matter and thus provides a method to directly measure D/H ratios of such phases even in the presence of organics [7]. We report preliminary measurements of particles from Ryugu and the Orgueil meteorite with this method; the results confirm the Cs-based measurements that present-day H_2O in Ryugu is D-rich and reveal an isotopic difference between Ryugu and CIs masked by larger errors in the prior investigation [6].

Methods: We analyzed two particles from Hayabusa2's first touch-down site, A0079 and A0169, as well as fragments of the Orgueil meteorite. Small (10s of μm) fragments were pressed flat onto clean Au foils for analysis in the Carnegie NanoSIMS 50L ion microprobe. We used a Hyperion (Oregon Physics) RF plasma source to generate secondary ions of H^+, D^+ and $^{12}C^+$. The 1 nA (~1-μm) O^- beam was rastered over samples and measurements made in imaging mode. A suite of terrestrial hydrated silicates (mostly amphiboles) was used to correct for instrumental fractionation (F=-337 ±70 ‰, 1σ).

Results and Discussion: We measured 8 Ryugu fragments and 6 Orgueil grains under identical conditions. Although the measurement resolution was much smaller than the analyzed particles, no isotopic heterogeneity was observed in any of the samples outside analytical errors (e.g., Fig. 1). Given that the OM in Ryugu samples and CCs is highly heterogeneous in D/H on micron scales, this both supports that the measurement technique indeed samples the phyllosilicates with negligible contribution from OM, and that the phyllosilicates have uniform D/H within the measurement precision.

The Ryugu samples (Fig. 2) all show slight D-enrichments, relative to terrestrial, with an average composition of $\delta D = +209 \pm 44$ ‰ ($2\sigma_{mean}$). In contrast, the Orgueil grains show slightly lower D/H, with an average $\delta D = +18 \pm 26$ ‰ ($2\sigma_{mean}$). Note that our Orgueil value is somewhat higher than that reported in a previous study that also used an O^- primary beam [8], which may reflect an issue with standardization with one or both studies. The relative difference between Ryugu and Orgueil grains is robust, however. Moreover, the H^+ secondary ion count rates of the Orgueil samples were systematically higher (by factors of up to ~1.8) than those of the Ryugu grains. This is consistent with bulk measurements indicating that Ryugu is depleted in H_2O relative to CIs by roughly a factor of two [3]. Thermogravimetric analysis indicates the difference lies in a lack of interlayer water in saponite grains in Ryugu and it was suggested that either the Ryugu surface samples lost this interlayer water to space and/or the CI meteorites gained theirs by terrestrial contamination. A lower D/H ratio for Orgueil water would seem to support the latter interpretation. However, we note that OM in Ryugu appears to be less D-rich than in CI chondrites [9], which is furthermore less D-rich than in CR chondrites [1] and in comet 67P [10]. Both CIs and Ryugu have experienced more aqueous alteration than CRs. If the Ryugu and CI parent asteroids accreted with OM similarly D-rich to that of CRs, the H isotope data are consistent with an initially D-poor water component (similar to that inferred for CM chondrites, for example, [1,5]) that subsequently exchanged with the D-rich organics [1]. In this case, the higher D/H of Ryugu water and lower D/H of Ryugu OM compared to Orgueil would point to more extensive exchange on the former's parent body. Fully deconvolving the effects of contamination from isotopic exchange on parent bodies is not yet possible with the very limited Ryugu datasets available so far.

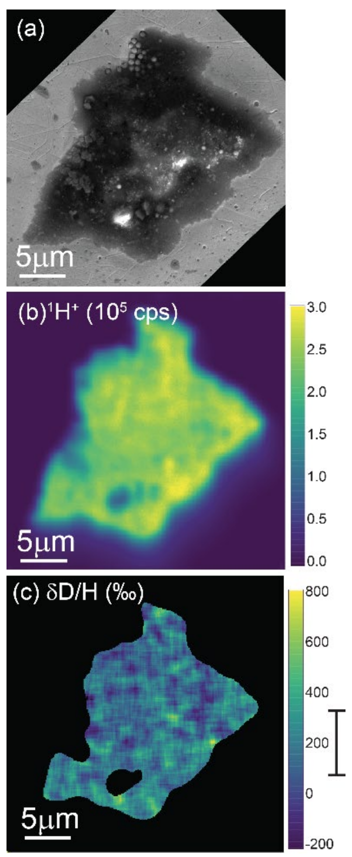

Fig 1. (a) SEM, (b) NanoSIMS H^+, (c) NanoSIMS δD/H images of a Ryugu particle. Error bar on (c) indicates average and standard deviation of grain.

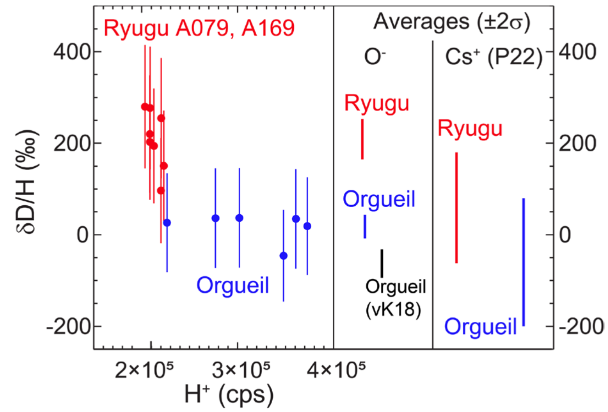

Fig. 2. Left: δD plotted versus H^+ count rate for Ryugu and Orgueil grains measured here with an O^- primary ion beam. Right: Average values for Ryugu and Orgueil grains are compared with data from [8] ("vK18") and [6] ("P22").

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