

^1H and ^{13}C Solid state Nuclear Magnetic Resonance (NMR) spectroscopy of an HCl extracted Ryugu C0002 particle

G. D. Cody¹, H. Yabuta², and the Hayabusa2-initial-analysis IOM team

¹Earth and Planets Laboratory, Carnegie Institute for Science, Washington, DC, USA

²Hiroshima University, Hiroshima, Japan

Introduction: ^1H and ^{13}C solid state NMR studies of extraterrestrial organic solids (Insoluble Organic Matter, IOM) in carbonaceous chondritic meteorites has the potential to reveal the extent of IOM's molecular evolution that occurred due to parent body processing (largely hydrothermal) in the interior of the original planetesimal from which the meteorite was derived. For example ^1H and ^{13}C NMR studies of IOM from CR, CI, CM, and an ungrouped C meteorites (Tagish Lake, TL) reveal that there is a wide range of molecular evolution where the least evolved was the CR IOM and the degree of molecular evolution increased from CI to CM to TL (Cody and Alexander, 2005). Subsequent NMR studies of discrete TL clasts with differing degrees of alteration revealed a high degree of molecular evolution across them (Herd et al., 2011). In all previous studies, relatively large (10's of mg) samples of pure IOM were available (note for typical CC meteorites, recoverable IOM constitutes ~ 1 wt % of the meteorite, 10 mg of IOM would require ~ 1gm of meteorite). For studies of Ryugu we were provided with a single particle that had been treated with aqueous HCL (to remove any carbonate) from C0002 that was ~ 1 mg where in principle 10 ng of IOM is expected. Notwithstanding the obvious challenges we endeavored to see what could be seen.

Experimental: All NMR experiments were performed at the W. M. Keck Solid State NMR facility at the Earth and Planets Laboratory at a static magnetic field of 7.05 Tesla. ^1H NMR analysis was performed using 2.5 mm rotor diameter Magic Angle Spinning (MAS) probe with the resonant frequency of ^1H being 300 MHz. The samples were spun at 22 KHz to reduce line broadening associated with H dipolar coupling. In order to reduce ^1H background signal arising from hydrogen outside the rotor we applied the DEPTH pulse sequence. The rotors capable of spinning faster than 20 KHz use endcaps and drive tips made of an aromatic polymer, Torlon, that is inside the rotor and will contribute some background ^1H signal. This background signal is generally negligible with 10-20 mg of pure organic matter. With the very small Ryugu sample it was expected and observed that the Torlon's ^1H back ground signal would be substantial. ^{13}C solid state NMR was attempted using a 5 mm probe (with MAS = 11.5 KHz) with Teflon (no H) inserts and a background suppression pulse scheme before Variable Amplitude Cross Polarization to maximize signal. We were unable to obtain any ^{13}C signal which is not unexpected given how little organic carbon is in a 1 mg Ryugu sample. We are pleased to report that no sample was lost during transfer into and out of both rotors and the sample was returned to Japan intact and unperturbed by the analysis. Thus the sample handling protocols adopted were sufficient.

Results: As expected the ^1H NMR signal is dominated by ^1H in the aromatic polymer, Torlon (Fig.1), at 7.1 ppm. We do detect a ^1H NMR signal at 1.3 ppm that arises from the Ryugu particle. In previous ^1H studies of pure IOM, aliphatic H appears at 1.3 ppm, so it may be that we are detecting Ryugu's aliphatic H. Note that IOM's aromatic H peak lies exactly at 7.1 ppm so it coincides with the background signal. It is now known that Ryugu mineralogy contains considerable amounts of saponitic clays, with two ^1H peaks at 4 and 0.35 ppm (Levin et al. 2004), thus the H from this clay is expected to be ~ 10 X that in IOM. However we don't see any H's from saponitic clay (Fig. 1). The most likely explanation is that the iron content of clays in the Ryugu sample are high enough that paramagnetic Fe "spoils" the signal from saponite H's and as IOM largely exists in the matrix as discrete organic grains, IOM signal persists. ^1H NMR of natural montmorillonite exhibits no signal due to Fe cations in its structure (Levin et al. 2004).

It is tempting to subtract the background signal from the bkgd+Ryugu particle, when one does this one finds that the line width of the Torlon is slightly greater than that of Torlon+Ryugu signal such that obvious spectra subtraction artifacts eventually arise and place a maximum constraint on how much

background subtraction can be performed, without this constraint one could range from majority aromatic-H to nearly 100 % aliphatic-H, neither case having been observed in any previous studies of type 1 and 2 chondritic IOM. Previous ^1H NMR analyses of IOM (Cody and Alexander, 2005; Herd et al. 2011) have been shown that there is a strong linear correlation between the Fraction of either aliphatic or aromatic H ($F_{\text{ARO-H}}$) with atomic H/C (*100) (see Fig.2) and with the fraction of aromatic carbon ($F_{\text{ARO-C}}$). Thus, using the restriction of maximum background subtraction we can place a minimum constraint on $F_{\text{ARO-H}}$ of 0.5 (there is no restriction on how large $F_{\text{ARO-H}}$ could be beyond assuming that there was no Torlon background). This places a maximum constraint of H/C*100 being 58 (there is no constraint on how low H/C*100 could be). Similarly, we can constrain a minimum as to how low $F_{\text{ARO-C}}$ could be at 0.64 (the only constraint as to how high it could be is controlled by the 1.3 ppm feature). These values would suggest that Ryugu's IOM has slightly greater molecular evolution than what has been observed in CM and CI derived IOM (Cody and Alexander 2005), but much less than observed for the most molecularly evolved Tagish Lake IOM (Fig. 2).

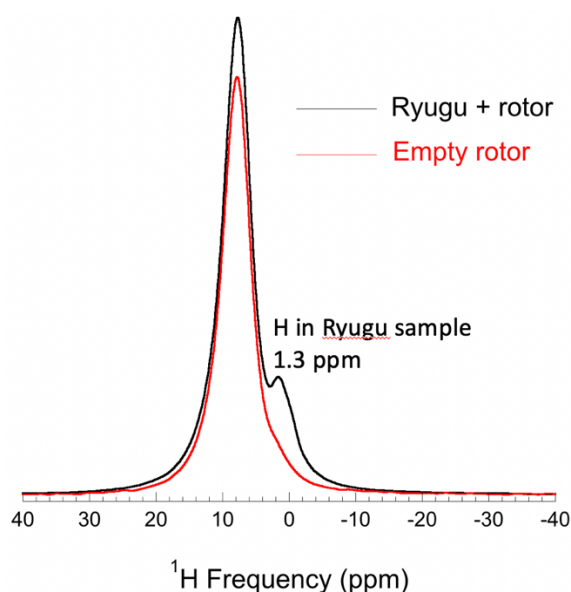


Figure 1: ^1H solid state NMR spectrum of 1 mg Ryugu particle from Chamber C (black). The background signal from Torlon is in Red

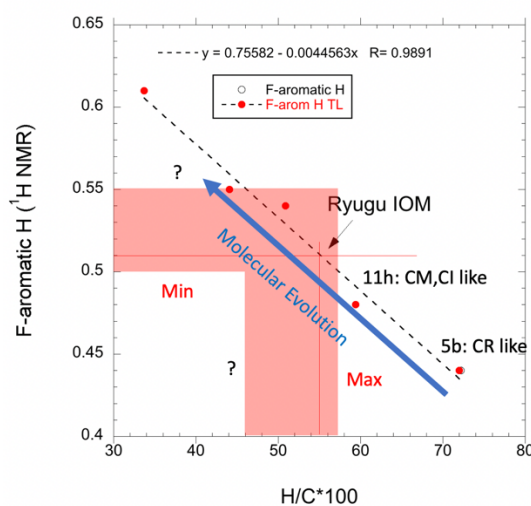


Figure 2: Background subtraction reveals a minimum $F_{\text{ARO-H}}$ and a maximum H/C. The red circles are values for IOM from the different Tagish Lake clasts. The red lines highlight an equally possible Ryugu composition

This study demonstrates that it is possible to obtain ^1H NMR spectra of Ryugu samples. In the future, if it were possible to obtain 100 mg of Ryugu particles, 1 mg of pure IOM could be isolated. This would increase the ^1H signal by 100 X vastly reducing the background signal. We have obtained fairly high quality ^{13}C NMR spectra on mg quantities of IOM, so additional molecular information would be obtained directly. Alternatively, if 20 mg of HCL extracted Ryugu particles were available (our 2.5 mm rotors can only handle 20 mg) these could be analyzed directly where the ^1H signal would be ~ 20 X that observed in Fig. 1. The advantage to this later approach would be that NMR is non-destructive and the sample would be available for other analyses by other researchers.

References:

Cody, G.D. and Alexander, C.M.O.D. (2005) NMR studies of chemical structural variation of insoluble organic matter from different carbonaceous chondrite groups. *Geochimica et Cosmochimica Acta* 69, 1085-1097.

Herd, C.D.K., et al. (2011) Origin and evolution of prebiotic organic matter as inferred from the Tagish Lake meteorite. *Science-SOM* 332.

Levin et al. (2004) *J. Applied Physics*, 96, 5685