

Nitrogen isotopes in Ryugu return samples revealed by the stepwise combustion analysis, in comparison with CI falls and Antarctic finds

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Nitrogen isotope ratio is a powerful tool in cosmochemistry to decipher the origin and evolution of planetary materials. The nitrogen isotope ratio $^{15}\text{N}/^{14}\text{N}$, usually expressed by the delta notation, $\delta^{15}\text{N} \equiv [(^{15}\text{N}/^{14}\text{N})/(^{15}\text{N}/^{14}\text{N})_{\text{AIR}} - 1] \times 1000$ (‰), exhibits large variations among different meteorites (Fig. 1). The isotope ratio of nitrogen, being a typical volatile element, is particularly useful to constrain the formation and evolution processes of planetary atmosphere for Earth and other rocky planets. Viable Earth formation models assume that CI/CM-like volatile-rich carbonaceous chondrites may have contributed as one of the important volatile sources for Earth, if not entirely on the source for the rocky body of this planet. CI chondrites, the most volatile-rich chondritic group known so far, exhibit $\delta^{15}\text{N}$ values typically around +40 ‰. The higher $\delta^{15}\text{N}$ values for the CI chondrites than for the present Earth atmosphere may impose important constraints on the formation and evolution history of the Earth atmosphere.

The texture and mineralogical composition of Ryugu samples are similar to CI chondrites. Three fall meteorites categorized as CI chondrites, Alais, Ivuna and Orgueil, have been studied so far for nitrogen isotopes. However, recent search on the vast stock of Antarctic meteorites has revealed that there exist several Antarctic meteorites which exhibit similar texture and mineralogical composition with the fall CI chondrites. Though similar, these potential CI Antarctic meteorites still exhibit marked difference from the CI falls, particularly from the volatile-element points of view: The majority of phyllosilicates are dehydrated in these Antarctic CI meteorites, while the phyllosilicates of CI falls mostly remain hydrated [4]. Fig. 2 compares bulk nitrogen isotope composition of Ryugu samples with those of CI chondrites, falls (Alais, Ivuna and Orgueil) and an Antarctic find (Y-980115). Interestingly, the $\delta^{15}\text{N}$ values are correlated with the nitrogen concentrations: lower the concentration, lower the $\delta^{15}\text{N}$ value. Note that this correlation is not compatible with the one we normally expect to occur by Rayleigh-distillation type devolatilization process, nor by addition of a terrestrial contamination at different degrees. Apparently, an unknown isotope fractionation (or mixing) effect in the nitrogen isotope composition has emerged among the CI-chondrite family.

The stepwise analyses may provide isotope “fingerprints” to compare the identities of planetary materials. By this method, we may distinguish possible endmembers co-existing in the samples. Fig. 3 demonstrates the usefulness of this method, for example, by the profiles obtained from a Ryugu bulk sample, compared with the one for CI chondrite Orgueil. These profiles provide information, not only the bulk $\delta^{15}\text{N}$ value and bulk N and C concentrations, but include points such as, (a) presence of a nitrogen component easily combustile at low (>200°C) temperatures with $\delta^{15}\text{N} < +10$ ‰, (b) a component released

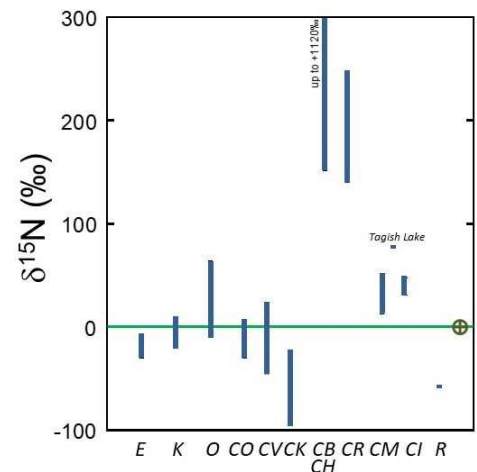


Fig 1. Bulk nitrogen isotope composition among different meteorites. Compilation by Hashizume (2015) [1]. Important isotope data beyond this range include protosolar composition (-380 ‰; Marty et al, 2011 [2]) or cometary range (+600 - +1000‰; Marty et al, 2016 [3])

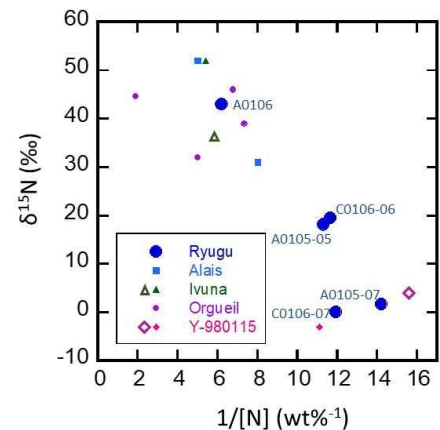


Fig 2. Bulk nitrogen isotope composition of Ryugu samples and CI chondrites. Ryugu data labelled A0105-07 and C0106-07 are reported in [5] (Ibaraki data); A0105-05 and C0106-06 in [6] (Nancy data); A0106 in [7] (JAMSTEC data). The other solid marks are literature bulk data for CI chondrites from [8-13]. Open marks (Ivuna and Y-980115) are sums of unpublished stepwise combustion data recently acquired at Ibaraki Univ.

spike-wise at $\sim 500^{\circ}\text{C}$ with $\delta^{15}\text{N} \ll 0$ ‰, which is inferred to be hosted by presolar nano-diamonds, (c) one released at $600\text{--}800^{\circ}\text{C}$ exhibits a plateau $\delta^{15}\text{N}$ value of $+17$ ‰, and (d) finally the one released at 1100°C and above with a $\delta^{15}\text{N}$ value as low as -20 ‰. Apparently, nitrogen in Ryugu consist of several components with distinct origins. The combustion profile of Orgueil, though shows partially similar isotope signature with Ryugu, for example the one presumably from presolar microdiamonds, exhibits generally $\delta^{15}\text{N}$ higher than Ryugu by several tens of ‰, and higher N concentrations. The differences are particularly prominent at low temperature range below 600°C , which is generally considered to be the range where N from the organic matter is released. Seemingly the organic matter with $\delta^{15}\text{N}$ values as high as $+60$ ‰ is missing in Ryugu, which could correspond to the “missing component” inferred by comparing the bulk composition for samples belonging to the CI chondrite family (Fig. 2). It is worth to note that, though the missing component could be inferred to be an organic component from the combustion temperature, it seems to be decoupled with the bulk of carbon, and could be a component with a peculiar chemical composition with much higher N/C ratios than the bulk composition.

In this presentation, we will compare the stepwise combustion profiles obtained for Ryugu, with those of Ivuna and Y-980115 recently obtained using the same facility equipped at Ibaraki University. Though part of the Ryugu data (A0105-07 and C0106-07) exhibit similar bulk nitrogen concentrations and $\delta^{15}\text{N}$ values with Y-980115, we will demonstrate that the combustion profiles appear quite different, possibly suggesting that the N isotope evolution mechanism could be different between these two kinds of CI-like samples.

References

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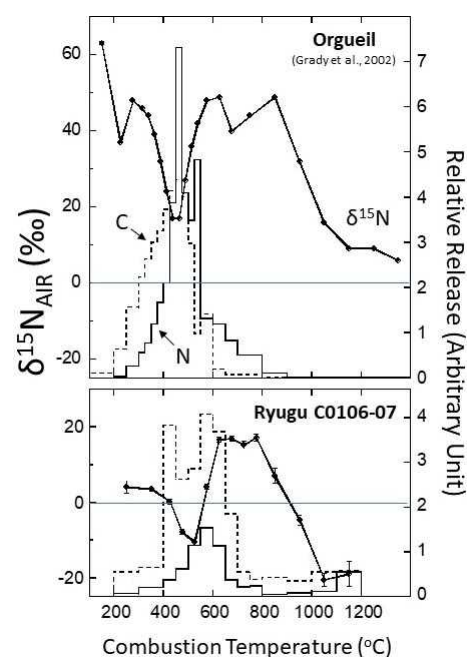


Fig 3. Comparison of stepwise combustion profiles for Ryugu sample C0106-07 (btm) obtained at Ibaraki Univ, and literature data [11] for Orgueil (top). The concentrations are plotted in arbitrary unit, although the areas of the bars between different temperature ranges, and also between the two samples for the same element correctly represent the relative concentrations.