Ryugu's volatiles investigated using stepped combustion and EGA methods

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Samples of the asteroid Ryugu collected by the Hayabusa 2 mission [e.g., 1-4] provide an excellent opportunity to undertake a comparative study for volatiles (e.g., H, C. N, S) measured in meteorites of similar type. This allows for a better understanding of the evolution of the meteoritic material during their transition through the atmosphere and residence on the surface of the Earth. In this study, we present the abundances and isotopic compositions of C, N and some noble gases in a Hayabusa 2 sample A0219 (as collaborative research under the Phase2 Kochi curation activity) and three CI meteorites (Orgueil, Ivuna and Alais). These measurements were performed using stepped combustion QEGA (Quantitative Evolved Gas Analysis) methods. It is important to note that utmost care has been taken to avoid any exposure of Hayabusa 2 material to the terrestrial atmosphere, from the time of the recovery of the sample capsule in Australia to sample allocation and preparation (in gloves box filled with pure N_2) and loading (with portable gate valve) for analysis by the Finesse instrument [5, 6] at the Open University. The sample aliquots used for the stepped combustion and QEGA were 2 and 0.5 mg respectively.

1. **Hydrogen.** Release of H_2 from A0219 during EGA occurs over a broad temperature range (400-1000 °C) with the major peak at 730 °C, similar to what is observed for the three CIs and seems to be associated with decomposition/oxidation of the organic macromolecular material. The total concentration (0.3 wt.%) of the molecular hydrogen in A0219 is also similar to that found in other CIs.

2. **Water.** In contrast to all other CIs analysed, the release of H_2O in A0219 has a single peak with maximum at ~550 °C: for Orgueil, Ivuna and Alais, the H_2O release is bimodal with an additional (apart from that at 530-570 °C) peak at low (~250 °C) temperature (Fig.1). The peak at 530-570 °C is thought to be associated with structural transformation of phyllosilicates at which their hydroxyl groups are released in the form of water. The low temperature peaks in CIs can be related to the adsorbed and/or hydroxide decomposition water release, associated with terrestrial weathering. In another study, the Hyabusa 2 sample analysed by TG-MS [7] showed a small peak of water at 100 °C, which was taken as evidence of heating on the surface of the asteroid to be limited to below 100 °C. However, the results here (Fig. 1) show no measurable water release below ~300 °C; the quadrupole MS signal at these temperatures is at the background level (<100) cps. As saponite can readily resorb water from atmosphere, it is possible that the release at 100 °C reported by Yokoyama et al. [6] is terrestrial contamination, and that the samples have been heated on the Ryugu's surface to temperatures of up to 300 °C. The total water content determined in A0219 (7.6±1.5 wt. %) is similar to that published for other Hayabusa 2 samples [6].

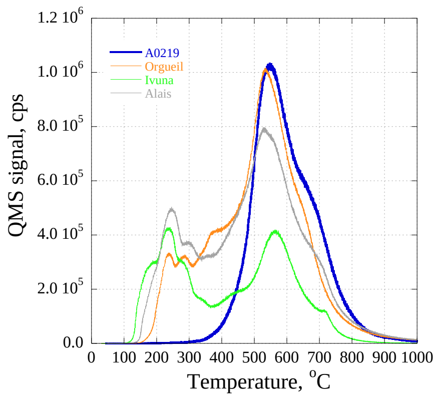

Figure 1. Release pattern of H_2O.

3. **Carbon.** Stepped combustion results clearly indicate that most of carbon in Hayabusa 2 (as in other CIs [8]) is associated with the macromolecular organic material and carbonates (Fig. 2). CO_2 from the latter is released at ~600 °C, characterised by a relatively high $\delta^{13}C$ values (up to 80‰) and present in CIs in variable amounts. In that sense, A0219 is not different from other CIs, though its carbonate concentration is relatively high. The petrographic studies of the Hayabusa 2 samples [6, 8] confirm the presence of Ca, Ma and Fe carbonates. Clearly, A0219 contains very little, if any, presolar SiC, signature of which (~1200 ‰ in its pure form) is often seen in CIs as enhanced $\delta^{13}C$ (up to few hundred per mile) at 1100-1300° C. EGA data show that carbon is released as both CO_2 at relatively low T and CO at higher T. Apart from decomposition of carbonates, these gases appear to be a result of oxidation of organic material in chemical reaction of the latter with the oxygen-bearing minerals. The total range of the carbon release is similar to that observed for molecular hydrogen confirming that all the species are associated with the macromolecular organics. The

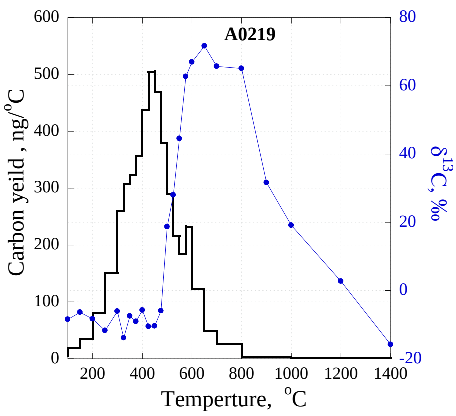

Figure 2. Release of C and $\delta^{13}C$ variations during stepped combustion.

total concentration of carbon determined by stepped combustion and QEGA are 6.3 and 4.6 wt. %, respectively that are within the range observed for CIs.

4. **Nitrogen.** During stepped combustion, nitrogen release is correlated with that of carbon indicating that it is one of the major constituents (along with C and H) of the macromolecular material. This is observed for the Hayabusa 2 and all CI samples. The variations in $\delta^{15}N$ in the temperature steps are also similar to those seen in other CIs (Fig. 3). In particular a characteristic feature of the variations (along with the presence of the relatively isotopically heavy organic component) is the excursion of the $\delta^{15}N$ to the isotopically light values at ~400 °C that could be explained by contribution from presolar nanodiamonds, pure separates of which have $\delta^{15}N$ ~-350 ‰. However, the calculated concentration of the nanodiamonds in the Hayabusa 2 sample using two-component mixing model with the isotopically heavy N shown by the dashed line (Fig. 3) and $\delta^{15}N$ = -350 ‰ assuming 1 % of the N in the nanodiamonds is significantly higher (by a factor of 2-3) than in fact observed in the most primitive meteorites. The same is true for Orgueil and Tagish Lake [8]. Therefore, there must be another more significant source of the isotopically light N component (possibly phase Q) with isotopic composition of N as light as the solar values ($\delta^{15}N$ ~-400 ‰), and which is oxidised in the same temperature range as nanodiamonds [5]. Nitrogen could not be identified by EGA because of the dominant presence of CO at m/z=28.

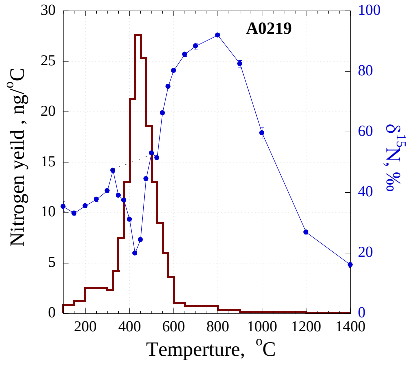

Figure 3. Release of N and $\delta^{15}N$ variations during stepped combustion.

5. **Sulphur.** Compared to all Cis, A0219 contains almost no sulphur. It is released at 300 °C and its estimated concentration is ~1.2 ppm, while CIs contain a few wt. % of sulphur. It is a surprising result and the reason for such a low concentration is not completely clear but may reflect sample heterogeneity. Further analyses need to confirm it. Only a part of sulphur in CIs is associated with terrestrial contamination. It follows from multicomponent sources of its release observed over a wide temperature range including elemental, organic, sulphite and sulphide sulphur as well as from its isotopic composition [10]. Investigation of other Hayabusa 2 samples by TG-MS [7] also indicated that the SO_2 signal is very low though petrographic data showed the presence of different sulphide minerals [7, 8]. On the other hand, in some works [11] it was suggested that most of sulphur in the meteorites is due to terrestrial contamination. Therefore, the low S concentration in the Hayabusa 2 samples is arguably as a result of the absence of any terrestrial contamination.

6. **Noble gases.** The ^{4}He, ^{20}Ne and ^{36}Ar relative abundances in A0219 correspond to a mixture of solar and planetary (Q) components. The isotopic composition of Ne shows a very small contribution of the cosmogenic component: most of the experimental points plots on the solar Ne fractionation line which is also a mixture of the solar and Q Ne, so that a contribution of the latter cannot be excluded. The data for other Hayabusa 2 grains [9] show Ne isotopic composition both without and with some contribution of the cosmogenic component. The A0219 material and other Hayabusa 2 grains with very little cosmogenic Ne contribution appear to have been exposed to solar wind radiation for a relatively short time being buried at a depth where galactic cosmic rays cannot penetrate for a longer time.

Conclusions. The EGA indicates that the A019 sample does not contain a low-temperature water release suggesting that its presence in all other CIs is due to terrestrial contamination. The very low sulphur content in the sample may also be an indication that sulphur in other CIs is also mostly due to terrestrial contamination. The A0219 Hayabusa 2 sample shows many features in C, N and noble gases abundance and isotopic compositions similar to those observed in CI chondrites. Carbonates concentration in A0219 is relatively high compared to other CIs. Hayabusa 2 definitely belong to the CI meteorite clan.

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