IRON VALENCE STATE AND MINERALOGY OF GRAINS FROM ASTEROID RYUGU. J.-C. Viennet[1], M. Roskosz[1], P. Beck[2], E.E. Alp[3], B. Lavina[3,4], M.Y. Hu[3], J. Zhao[3], T. Nakamura[5], K. Amano[5], M. Kikuiri[5], T. Morita[5], E. Kagawa[5], H. Yurimoto[6], T. Noguchi[7], R. Okazaki[8], H. Yabuta[9], H. Naraoka[8], K. Sakamoto[10], S. Tachibana[10,11], S. Watanabe[12], Y. Tsuda[10], and the Hayabusa2-initial-analysis Stone team.

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Introduction: Iron occurs under multiple valence state. As such it is used to trace geological processes that occurred on asteroids including thermal metamorphism and aqueous alteration. Observations of the mineralogy of carbonaceous chondrites have revealed the presence of mineral assemblages that are barely in thermodynamic equilibrium. Even at the micron-scale, iron is often present under multiple valence state in a wide range of minerals (primary or secondary in nature), including silicates, oxy-hydroxide, sulfides, sulfates, clay minerals and carbonates. It is therefore tricky to disentangle the different processes recorded by the iron mineralogy of chondritic materials. Furthermore, since most Fe-bearing phases are redox-sensitive, exposure to terrestrial atmosphere may also induce iron oxidation and additional, late modifications of the iron mineralogy. In this context, Hayabusa2 sampled Ryugu, an asteroid that did not suffer extensive thermal metamorphism, and returned rocks to Earth with no air exposure. It offers a unique opportunity to study the redox state of carbonaceous asteroids and evaluate the overall redox state of the most oxidized primitive rocks of the solar system.

Methods: Two coarse Ryugu samples (A0026 and C0061) where analyzed by Conventional and Synchrotron Mössbauer Spectroscopies (MS and SMS respectively). A0026 was collected at the first touchdown site, and C0061 from the second touchdown site. These samples were glued to an iron-free glass rod and then placed in sealed small plastic containers under inert nitrogen atmosphere. All measurements were performed through these containers. Samples were never exposed to air. Samples were first analyzed by MS. X-ray diffraction maps were collected using the focused beam to probe the samples homogeneity and better target SMS measurements. Then, SMS and polarized SMS were collected using unfocussed and focused X-ray beams to obtain bulk and spatially-resolved information.

The MS measurements were performed in transmission mode using a constant acceleration spectrometer. The line widths used to fit the spectra were reasonably wide to get a good fit, without invoking a gaussian distribution of hyperfine parameters. The SMS measurements were conducted at Sector 3-ID-B of the Advanced Photon Source (APS). Some measurements were performed with the samples inside a permanent magnet with a magnetic field of 0.78 T, where the magnetic field direction is perpendicular to both the X-ray beam direction and its polarization vector. Though generally neglected, the recoil-free fraction of iron atoms is slightly different for Fe^{2+} and Fe^{3+} in silicates. A typical reasonable correction was applied [1, 2] on the areas of the quadrupole doublets to estimate the redox ratios of clays based. The difference with uncorrected values was still within the typical error associated with redox determination based on Mössbauer spectra, typically estimated to 3-5%.

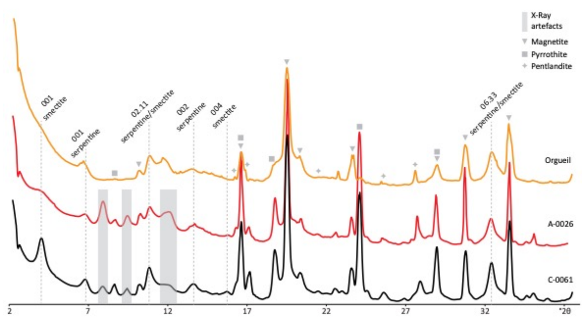

Fig. 1: Bulk X-Ray diffraction patterns of Orgueil, grains A-0026 and C-0061 from Ryugu.

Results: Based on XRD patterns, the major phases present in grains A0026 and C0061 are magnetite, pyrrhotite, pentlandite and clay minerals (Fig. 1). Clay minerals are Mg-rich based on their 02.11 and 06.33 reflections at 4.59 and 1.537 Å, respectively. They contain significant amount of serpentine and smectite-rich minerals. Turning to the redox state of clays, slight variations on the 02.11 and 06.33 reflections is observed between grains A0026 and C0061. These reflections are shifted towards higher angles for the A0026 and Orgueil as compared to C0061 (Fig.1). This shift may suggest a higher Fe^{3+} content in octahedral and/or tetrahedral position in smectite layers found in Orgueil and grain A0026 [3].

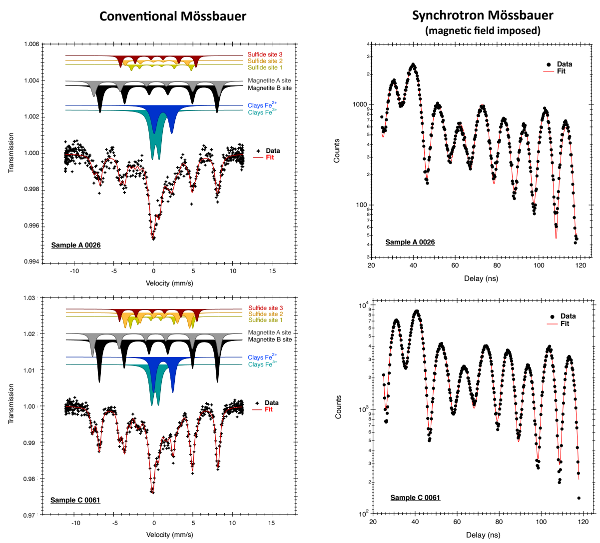

Fig. 2: Conventional (right panels) and polarized synchrotron (left panels) Mössbauer spectra of the grain A-0026 (on top) and C-0061 (bottom). Best fits to the data are shown in red.

Conventional Mössbauer spectra collected on grain C0061 and A0026 are dominated by magnetite and pyrrhotite sextets (Fig. 2). In the central part of the spectra, two clear quadrupole doublets due to paramagnetic Fe^{2+} and Fe^{3+} are observed in the two samples. The Fe^{2+} doublet is more intense in C0061 than in A0026 (Fig. 2). The fraction of iron present in each of these sites was derived: Magnetite concentrates about 40-50 at.% of the total iron, pyrrhotite ~15-30 at.% and silicates (and possibly oxyhydroxides) contain about 25-40 at.% of iron. These fractions vary from one grain to the other, and at the microscopic scale.

Because of the overlap of many different magnetically split components and the large variability of the typical signatures of magnetite and pyrrhotite, the determination of the redox ratios of paramagnetic phases (the two quadrupole doublets) has an elevated uncertainty. For this reason, SMS spectra were collected without and with a permanent external magnetic field (Fig. 2) because many magnetically split components are cancelled (all the $\Delta m=\pm1$ lines). For this reason, the surface ratio of the two quadrupole doublets is more reliable. From this fit to the data, the ratios are found to be Fe^{3+}/Fe_{tot} of 0.39 for grain C0064 and 0.52 for grain A0026.

Discussion: The magnetically split components assigned to iron in the tetrahedral (A) and octahedral (B) sites of magnetite present area ratios very close to the nominal stoichiometry of magnetite (1:2). This is a first notable difference with typical Orgueil signatures for which magnetite was found significantly more oxidized than this typical stoichiometry (Fig.3).

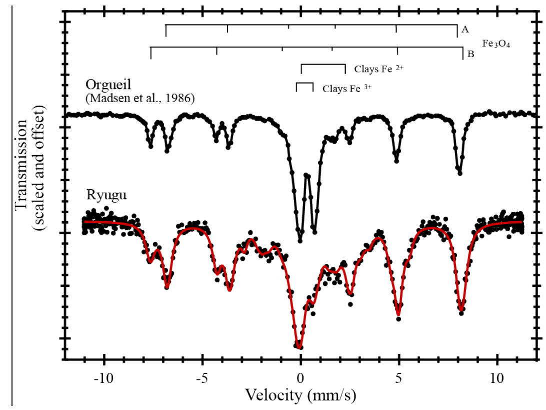

Fig. 3: Comparison of conventional Mössbauer spectra of the Meteorite of Orgueil and Ryugu grain (A-0026).

The redox ratios (Fe^{3+}/Fe_{tot}) are also significantly lower than those measured in Orgueil (typically ~0.8-0.9) and Murchison (typically ~0.7). The attribution of quadrupole doublets to particular minerals is not straightforward. While the Fe^{2+} is clearly attributed to clay minerals (ferrous iron in octahedral position), it is possible that a fraction of the Fe^{3+} measured could be accommodated in oxyhydroxides. This is the case in Orgueil, known to contain large amount of ferrihydrite [4, 5]. Yet, the total amount of water present in the Ryugu samples is low and analysis performed by the preliminary examination teams did not point to significant occurrence of such phase. For this reason, it is proposed that the measured Fe^{3+}/Fe_{tot} is primarily the redox ratio of clay minerals present in Ryugu.

Conclusions: We provide the first macroscopic, bulk estimate of the mineralogy, relative abundances and redox state of iron-bearing minerals from Ryugu before any exposure to terrestrial atmosphere. Contrary to Orgueil or Tagish Lake meteorites, magnetites from Ryugu are stoichiometric and are not anomalously oxidized. The same holds for pyrrhotite that do not show trace of oxidation. Furthermore, clays from Ryugu are more reduced than typical CI and CM carbonaceous chondrites found on Earth so far. This strongly suggests that the terrestrial alteration of most primitive extraterrestrial samples is maybe even more pervasive than previously suggested. The Hayabusa2 samples are certainly the most pristine chondritic material analyzed to date and may represent the initial state of CI chondritic material.

References: [1] Dyar et al. (2008); [2] Roskosz et al. (2022); [3] Baron et al. (2016); [4] Madsen et al. (1986); [5] Tomeoka and Buseck (1988).