**RAMAN MICRO-SPECTROSCOPY OF HAYABUSA PARTICLES.** U. Böttger[1], C. Alwmark[2], S. Bajt[3], H. Busemann[4], J.D. Gilmour[4], U. Heitmann[5], H.-W. Hübers[1,6], M.M.M. Meier[2], S.G. Pavlov[1], U. Schade[7], N.H. Spring[4], I. Weber[5]. [1]Inst. of Planet. Res., DLR Berlin, Germany (ute.boettger@dlr.de), [2]Dept. of Geol., Univ. of Lund, Sweden, [3]Photon Sciences, DESY, Hamburg, Germany, [4] SEAES, Univ. of Manchester, UK, [5]Inst.f. Planet., WWU Münster, Germany, [6]Techn. Univ. Berlin, Germany, [7]Helmholtz-Zentrum Berlin (HZB), Germany.

**Introduction:** Material from the S-type asteroid 25143 Itokawa was successfully sampled by JAXA's Hayabusa-Mission and returned in 2010. The first studies [1-5] indicated that Itokawa consists of mostly petrologic type LL5-LL6 material.

In the scope of the 1st international AO a consortium study [6] was submitted to and accepted by JAXA for the analysis of noble gases in Itokawa samples. These noble gas studies were combined with Raman micro-spectroscopy, Infrared spectroscopy (IR), and synchrotron radiation X-ray tomographic microscopy (SRXTM) [7]. These methods yield mineralogy, grain density, and structure necessary to estimate the gas concentrations of potentially present cosmogenic, solar, trapped and radiogenic noble gases. Here the results of Raman micro-spectroscopy are presented.

**Samples:** JAXA provided seven particles to the consortium. Two particles embedded in epoxy (RA-QD002-0035, -0051) were already previously investigated by secondary ion mass spectrometry (SIMS) [4]. Two further particles were fragments of a larger particle (RA-QD002-0049-1, -4) examined by neutron-activation analysis [5], and remained under cover glass to be protected against loss and further contamination. These four particles had contact with the Earth's atmosphere. Three particles (RA-QD002-00158, -00187, -00197) were delivered in inert $N_2$ gas and had never been in contact with the atmosphere.

**Measurements:** All particles were investigated with a Witec Alpha 300 microRaman spectrometer. The laser excitation wavelength was 532 nm, the spectral resolution about 4 $cm^{-1}$. The spot size on the sample was approximately 1 µm. The polarization effects of the sample were taken into account by including at each point measurements at different positions of the polarizer. Each single measurement took 120 s. For scans the measurement time was 10 s per spectrum. The laser power on all samples was 200 µW, except of the particle #51 with 4 mW.

*Embedded particles*. Single spectra were measured with an 100x objective on different parts of the samples to identify the minerals. Additionally, as the surface was polished an automated scan was performed to demonstrate the distribution of the mineral phases.

*Particles under cover glass.* Single spectra were measured with a long-distance 10x objective through the cover glass that protected the particles against loss and contamination. Measurements were performed on the surface and in 10 µm depth to check the presence of zoning or inclusions.

*Particles in $N_2$ gas*. The samples in the $N_2$-filled container were measured with a long-distance 10x objective through a transparent Quartz glass port that replaced the original JAXA top cover. Single Raman spectra were collected from the samples for mineral identification. The samples were scanned manually covering the visible sample surface with a measurement time of 120 s or 240 s.

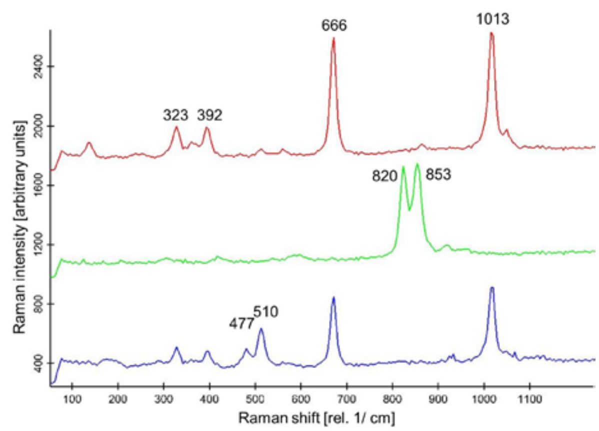


**Fig. 1:** Raman spectra measured on particle #51. (red – pyroxene; green – olivine; blue – plagioclase and pyroxene).

**Results and Discussion:** Typical Raman spectra measured on the Hayabusa samples are shown in Figure 1. Most of the samples/grains consist only of Mg-rich olivine. The Raman main lines of the olivine - doublet at around 820 $cm^{-1}$ and 853 $cm^{-1}$ - indicate that the olivines consist mainly of forsterite ($Mg_2SiO_4$). According to [8] and [9] it ranges between ($Fo_{60}$ – $Fo_{70}$. ± 10%) (see Figure 2).

For two samples (#51, #197) also pyroxene and plagioclase could be identified. Raman lines at around 323 $cm^{-1}$, 392 $cm^{-1}$, 666 $cm^{-1}$, and 1013 $cm^{-1}$ are characteristic for pyroxene [10]. Plagioclase has been identified using the Raman shifts around 477 $cm^{-1}$ and 510 $cm^{-1}$ of the symmetric T-O stretching and the O-T-O deformation modes in the T-O groups (T can be K, Ca, Na) characterizing the feldspar. According to Freeman et al. [11] it is probably K-feldspar.

In particle #35 micrometer-sized metal-rich grains were observed. The Raman spectra of these small inclusions are compatible with goethite. As this sample was in contact with the Earth's atmosphere, goethite might be an alteration product of, e.g., troilite. The presence of troilite in Itokawa grain #35 was deduced by former SEM measurements [3].

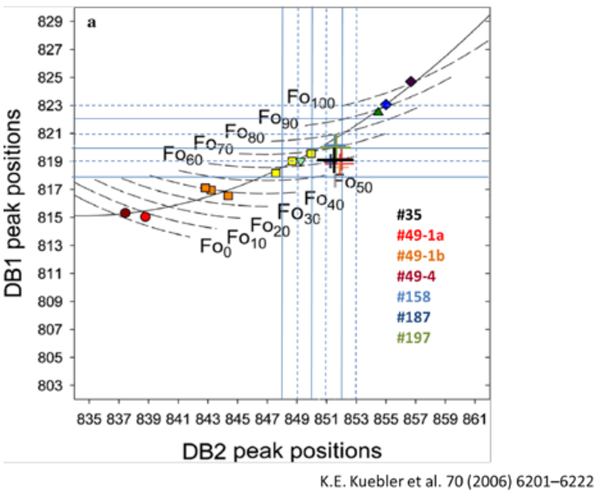


**Fig. 2:** Comparison of derived peak positions of the olivine doublet (shown by crosses) with two-peak calibration data sets of Kuebler et al. [8].

Particle *#197* was stored in inert gas and had thus never been in contact with the Earth's atmosphere. The particle consists of olivine, plagioclase, and pyroxene. An orientation map of olivine crystals was derived by the interpretation of the relative intensities of the olivine doublet that are directly dependent on the orientation of the plane of polarization of the olivine crystal. Except for one area, minor or no changes in orientation were detected, which is a hint that grain #197 consists of a single crystal instead of many small grains. The exceptional area corresponds to an edge of the crystal surface resulting in a jump in relative Raman shift intensities of the olivine doublet.

**Summary and Conclusions:** Confocal Raman micro-spectroscopy is effective for initial non-destructive structural and chemical analysis of samples from space probe missions, even if they are stored in sample containers in inert gas or vacuum. Different mineral phases could be distinguished for the samples. Phase surface maps with a spatial resolution of ~1 µm were reconstructed from Raman microscopic measurements.

Mg-rich olivine was identified for all samples. Pyroxene and plagioclase were identified for #51 and #197. Goethite, found in #35, could be an alteration product from a Fe–bearing mineral like troilite. Results of Raman measurements are consistent with an ordinary chondrite of the petrologic type LL5–LL6.

Problems arising during measurements were with the result of carbon and gold coating of the particles. This led to very high fluorescence strongly masking the mineral spectra. In cases of carbon coating, laser-induced heating due to coupling with the C of these small particles could influence the follow up noble gas analysis. Thus for carbon-coated particles very low laser power was applied for subsequent measurements (compare Measurement section).

For future analysis of extraterrestrial samples it is advisable to start with non-destructive methods like Raman or IR- spectroscopy before any manipulation of the samples such as polishing, coating or SIMS analysis is applied.

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**References:** [1] Nakamura T. et al. (2011) *Science, 333,* 1113-1116. [2] Nagao K. et al. (2011) *Science, 333,* 1128-1131. [3] Noguchi T. et al. (2011) *Science, 333,* 1121-1125. [4] Yurimoto H. et al. (2011) *Science, 333,* 1116-1119. [5] Ebihara M. et al. (2011) *Science, 333,* 1119-1121. [6] Busemann H. et al. (2013) *Lunar & Planetary Science Conference* XLIV, Abstract #2243. [7] Meier M.M.M. et al. (2014) *Lunar & Planetary Science Conference* (this meeting). [8] Kuebler, B. L. et al. (2006) *Geochimica et Cosmochimica Acta 70,* 6201–6222. [9] Gaisler S.V. et al. (2007) *J. Struct. Chem. Vol. 48,* No. 1, pp 61-65. [10] Wang A. et al. (2001) *Am. Min. Vol. 86,* 790-806. [11] Freeman J. et al. (2003) *Lunar & Planetary Science Conference XXXIV,* Abstract #1676.