SHOCK STAGE CLARIFICATION OF PLAGIOCLASE SAMPLES FROM ASTEROID ITOKAWA USING RAMAN AND CATHODOLUMINESCENCE MICROSCOPY AND SPECTROSCOPY: A REVIEW.

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Introduction: Materials subjected to shockwaves display characteristic and irreversible physical and chemical changes on both macroscopic and microscopic scales, depending on the applied shock strength. Various techniques for estimation of shock pressure or determination of shock stage have been developed and applied for the constituent minerals, especially feldspar. The shock pressures on the extraterrestrial materials have been mainly evaluated using the refractive index method, optical and scanning electron microscope for observation of characteristic features or structures derived from shock metamorphism and for identification of the paragenetic assembly of high-pressure minerals, X-ray diffraction analysis, IR spectroscopy and transmission electron microscope, but these methods above are not applicable to micrometer-sized particles consisted in the Hayabusa-samples.

According to Zolensky et al. ([1]-and references therein) shock metamorphism can cause irreversible mineralogical changes and reset chronologies. Therefore, failure to take shock history into proper account during the characterization can result in misleading interpretation. In this case, the evaluation of the shock stages presented in the selected materials can help us to avoid any incorrect data obtained from those samples, for instance.

Therefore, a new method for the shock pressure estimation was developed with high-spatial resolution within a few micrometers as a nondestructive analysis, and achieved a successful outcome on quantitative evaluation of shock pressure induced on alkali feldspar particles in meteorites as well as fine-grained astromaterials: A combination of Scanning Electron Microscope-Cathodoluminescence (SEM-CL) Microscopy and Spectroscopy and Raman Spectroscopy

Shock wave determination: *Micro-Raman Spectroscopy:* Recently, Micro-Raman analysis has been applied for micrometer-ordered plagioclase or maskelynite grain in meteorite to determine the shock stage, but semiquantitative. Raman spectra of shocked plagioclase and maskelynite consist of peaks at 505 and 590 cm^{-1} to the compression vibrations of four-member tetrahedral rings [2]. The shock-induced deformation of the plagioclase crystal lattice causes a decrease in intensity and an increase in luminescence background of these Raman peaks, which can be used as an indicator for shock stage determination. These Raman signals are, however, too weak to be applied as an indicator for shock barometer. For quantitative shock estimation, sufficient Raman signal should be detected using Micro-Raman spectroscopy under temperature-controlled conditions. High-pressure feldspar minerals show pronounced and weak Raman peaks 214, 283, 521, 539, 621, 655 and 761 cm^{-1} all of which intensity drastically increase with reducing sample temperature.

A plagioclase particle (RA-QD02-0025-01) returned by the Hayabusa spacecraft from asteroid Itokawa was selected for a Raman study by Gucsik et al. [3]. Raman spectral properties obtained at 514 nm (University of Johannesburg, South Africa) excitation show two Raman vibrations at 476 and 505 cm^{-1}, which are superimposed at relatively high background fluorescence. This indicates a highly distorted structure. In order to reduce the background fluorescence, Raman spectra were taken from two spectral regions such as 400-600 and 1100-1200 cm^{-1} using LabRam (Jena, Germany) facility at 638 nm excitation. Raman spectral properties exhibit three Raman bands centered at 476, 505 and 1009 cm^{-1} (Fig. 1a and b). According to McKeown [2], Raman peaks in albite at 476 cm^{-1} is related to the tetrahedral ring compression in ab-plane, at 505 cm^{-1} is assigned to compression of four-membered tetrahedral rings along c and a peak centered at 1009 cm^{-1} is associated with Si-tetrahedral base breathing (Fig. 1). Shock pressure-induced amorphization such as occurrence of maskelynite and its Raman signatures were not observed in the selected grain.

Cathodoluminescence: Cathodoluminescence (CL) is the emission of photons in the visible range from a material stimulated by an incident electron beam, being feasible for high-spatial-resolution (~1 µm) spectroscopy. CL studies for minerals, especially feldspar, have been conducted in planetary sciences to characterize the shock metamorphic effect in samples to identify high-pressure minerals. Although these previous studies reported CL features closely related to shock metamorphism, quantitative information on the shock pressure have not been provided. These days, we can elucidate shock-induced effects on the CL spectra of alkali feldspars. Consequently, CL spectroscopy can be used as a universal shock barometer with high spatial resolution of ~1 µm in a wide pressure range from 4.5 GPa to >40 GPa.

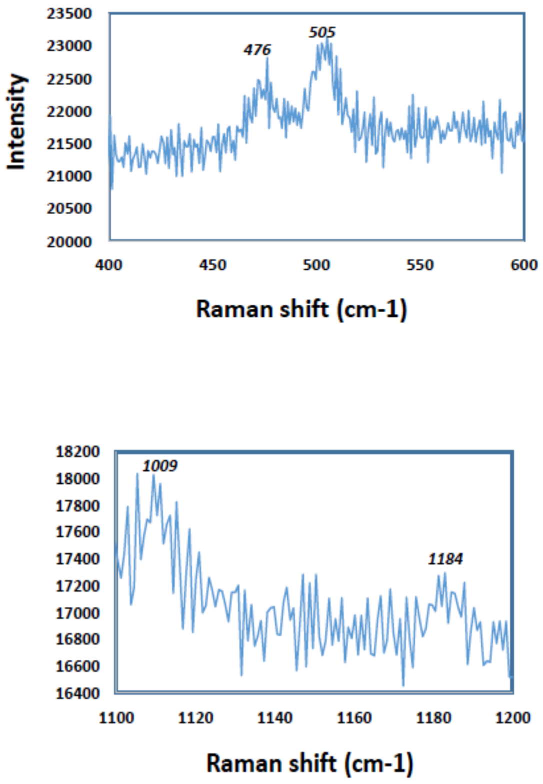

Figure 1. *Raman spectral features of the selected Itokawa-particle (RA-QD02-0025-01) (data from [3])*

According to Gucsik et al. (2017) cathodoluminescence spectral features of the Itokawa plagioclase sample (RA-QD02-0025-01) exhibit two emission centers: a broad band at around 450 (2.82 eV) and a shoulder peak at around 420 (3.04 eV) nm (Figs. 2a-c). Spectral composition after deconvolution shows two components at around 2.8 (defect center) and 3.0 eV (Ti-activator) [4,5].

Conclusion: This study above clearly demonstrates that a combination of Scanning Electron Microscope-Cathodoluminescence (SEM-CL) Microscopy and Spectroscopy and Raman Spectroscopy are a powerful, easy-to-use, and non-destructive method to study fine-grained astromaterilas and their shock wave history. This can apply for the further sample return missions such as OsirisRex or Hayabusa-2. This can also aid to interpret ESA Hera impact data in the near future.

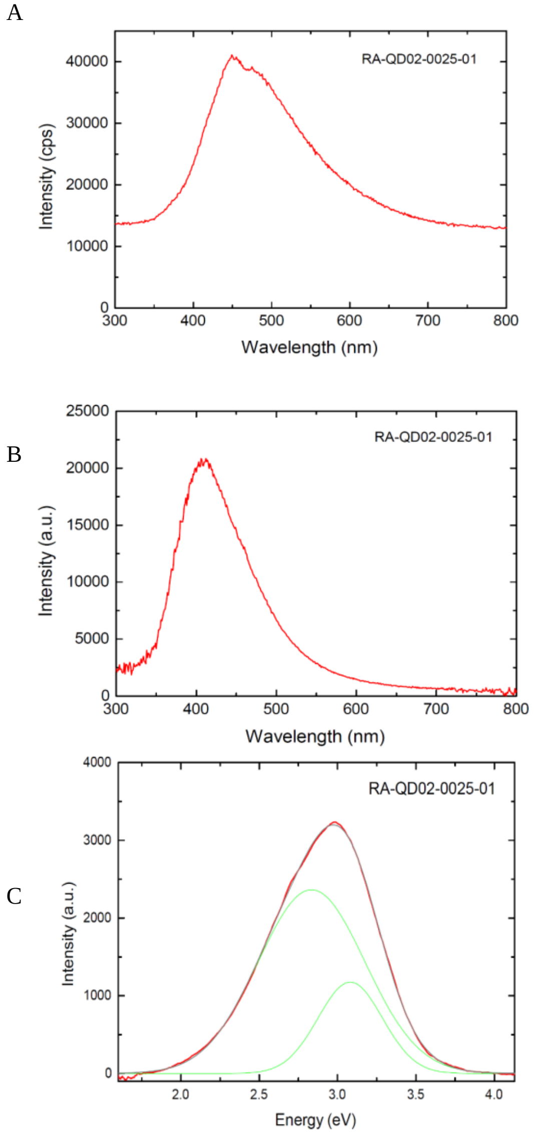

Figure 2. *Cathodoluminescence (SEM-CL) spectral features of the selected grain (RA-QD02-0025-01) from asteroid Itokawa showing measured (a), corrected (b) as well as deconvoluted (c) spectra (data from [3]).*

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