Uranium-Lead dating of Zagami phosphates by NanoSIMS. T. Morita[1], Y. Sano[2]*, M. Koike[2], S. Onda[2], N. Takahata[2], and H. Hiyagon[1], [1]Department of Earth and Planetary Physics, The University of Tokyo, (Hongo 7-3-1, Bunkyo-ku, Tokyo 113-8654, Japan, morita@g.ecc.u-tokyo.ac.jp), [2]Atmosphere and Ocean Research Institute, The University of Tokyo (Kashiwanoha 5-1-5, Kashiwa, Chiba 277-8564, Japan). *corresponding author (ysano@aori.u-tokyo.ac.jp)

Introduction: Shergottites are members of the SNC meteorites, which are thought to be impact ejecta from the planet Mars. They are basaltic achondrites possibly crystallized from a magma in Mars' crust and show geochemical variation from enriched to depleted incompatible element concentrations [1]. It is well documented that the enriched and intermediate types indicate radiometric age of 165-200 Ma, while the age of depleted type varies from 327 to 575 Ma [2]. Shergottites are grouped into three petrological types; olivine-phyric, basaltic and lherzolitic rocks [3]. Zagami and Shergotty are textually and mineralogically similar and belonging to enriched basaltic type with complex generation history [4]. Early attempt of U-Pb dating of these meteorites by chemical separation and TIMS instrument showed that leached residues and whole rocks of Shergotty yielded an isochron ^{238}U-^{206}Pb age of 200±4 Ma except for a few leaches susceptible to laboratory contamination [5]. On the other hand, leachate, residue and whole rock of Zagami suggested the ^{238}U-^{206}Pb age of 230±5 Ma. In 2001, ion microprobe U-Th-Pb dating of Shergotty phosphates was conducted by SHRIMP instrument and provided a formation age of 204±68 Ma based on ten apatite and three merrillite analyses [6], which is consistent with TIMS age of ~200 Ma. On the other hand, SHRIMP U-Pb dating of Zagami phosphates showed ~360 Ma [7], significantly older than TIMS age of ~230 Ma. In 2005, ^{238}U-^{206}Pb dating of Zagami by TIMS method suggested much younger age of 156±6 Ma based on selected residue fractions [8], while whole rock and leaches showed more radiogenic signature. In 2008, ^{207}Pb-^{206}Pb dating of Zagami gave an ancient age of 4048±17 Ma by MC-ICP-MS instrument after chemical separation [9]. The most recent results of ^{238}U-^{206}Pb age of Zagami phosphates was 153±81 Ma measured by Cameca IMS-1280 instrument [10]. The U-Pb ages of Zagami are, thus, significantly complex and not fully consistent in literatures. We present here U-Pb dating of Zagami phosphates by NanoSIMS.

Samples: The thin section sample (termed "normal Zagami" with coarse-grained mineral assembladge) was mounted on a slide glass with epoxy resin and polished until it was exposed through phosphate mid-sections to provide a flat surface for sputtering of secondary ions. The polished thin section was carbon coated and back-scattered electron images were obtained by SEM-EDX installed in Department of Earth and Planetary Physics, The University of Tokyo in order to locate calcium phosphate grains. Thirteen phosphate grains were identified with sizes ranging from 40 to 100 μm. Most grains are merrillite together with a few apatite. They have small inclusions or cracks.

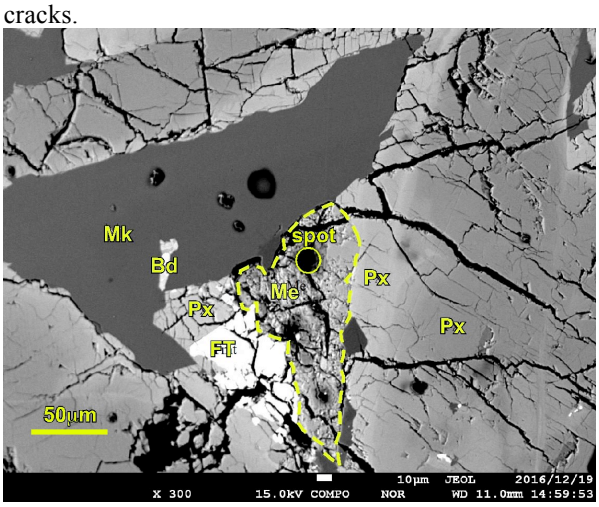

Figure 1. Back-scattered electron image of Zagami phosphate.

Typical image of phosphate grain is shown in Fig. 1. Merrillite (Me) occurs with maskelynite (Mk), pyroxene (Px), baddeleyite (Bd) and Fe-Ti oxides (FT).

Analytical Methods: The U–Pb dating was conducted using NanoSIMS 50 installed at the Atmosphere and Ocean Research Institute, The University of Tokyo. An approx. 10 nA $^{16}O^-$ primary ion beam with a spot diameter of approx. 15 μm is focused on the sample surface. Positive secondary ions are extracted with an accelerating voltage of 8 kV. For ^{238}U–^{206}Pb dating, $^{43}Ca^+$, $^{204}Pb^+$, $^{206}Pb^+$, $^{238}U^{16}O^+$ and $^{238}U^{16}O_2^+$ are collected simultaneously with a dual-collector-combined multi collection system (Hereafter called U-Pb procedure). Although ^{204}Pb abundance of the phosphates is so low that identification of the ^{204}Pb peak on mass spectra images is difficult, no isobaric interference was found in this mass range or the mass range over ^{206}Pb and ^{207}Pb with mass resolution of approx. 4100 at 1% peak height. For SIMS measurements, secondary U ions are extracted mainly as monoxide and dioxide, although Pb is emitted almost entirely as atomic ions. Calibrations must be applied to derive true

U/Pb ratios of samples from the secondary ion counts. We applied a quadratic relation that was derived originally for zircon dating [11] as follows:

$$(^{206}Pb^{+}/^{238}U^{16}O^{+}) = a\times(^{238}U^{16}O_2^{+}/^{238}U^{16}O^{+})^2 + b$$

In that equation, a and b are constants determined by correlation between observed $^{206}Pb^{+}/^{238}U^{16}O^{+}$ and $^{238}U^{16}O_2^{+}/^{238}U^{16}O^{+}$ of our standard apatite "PRAP" [12]. Uranium concentrations of analyzed spots are obtained by comparing the measured $^{238}UO^{+}/^{43}Ca^{+}$ ratios of the sample against those of the standard. After ^{238}U–^{206}Pb measurements, ^{207}Pb–^{206}Pb ages on the same spots were determined using single-collector mode, where the magnet was cyclically peak-stepped through $^{204}Pb^{+}$, $^{206}Pb^{+}$, and $^{207}Pb^{+}$ (Pb-Pb procedure). The pit depth was possibly less than 3 μm after the measurement, which is markedly smaller than the spot diameter. Experimental details were given elsewhere [13].

Results & Disucssion: We measured U concentrations, $^{238}U/^{206}Pb$, $^{207}Pb/^{206}Pb$, and $^{204}Pb/^{206}Pb$ ratios of fifteen spots on thirteen phosphate grains of Zagami. Two data sets of $^{204}Pb/^{206}Pb$ ratios were obtained by U-Pb and Pb-Pb procedures. They are consistent within 2σ error except for two spots. Observed U contents vary from 2.4 ppm to 9.5 ppm, very similar to 2-9 ppm measured by Cameca IMS-1280 [10]. Under the U-Pb procedure, $^{238}U/^{206}Pb$ ratios are ranging from 0.930 to 5.50, while the $^{204}Pb/^{206}Pb$ ratios from 0.0427 to 0.0649. There is a weak negative correlation between them. Based on the least-squares fitting using the York method, the relationship gives a $^{238}U/^{206}Pb$ isochron age of 164±240 Ma (MSWD=1.6; 95% confidence limit). This age is consistent with 153±81 Ma of Zagami phosphates measured by Cameca IMS-1280 [10], but youger than 360 Ma by SHRIMP [7]. Under the Pb-Pb procedure, the $^{207}Pb/^{206}Pb$ ratios change from 0.850 to 1.07, while the $^{204}Pb/^{206}Pb$ ratios from 0.0596 to 0.0827. There is no correlation between these ratios, which does not provide a $^{207}Pb/^{206}Pb$ isochron age. Next, we calculated a "total Pb/U isochron age" from a linear regression line in 3-D space ($^{238}U/^{206}Pb$-$^{207}Pb/^{206}Pb$-$^{204}Pb/^{206}Pb$) and Concordia curve. In the calculation we take an error weighted mean of two data sets of $^{204}Pb/^{206}Pb$ ratios by both procedures. The crucial advantage of this total isochron method is that it is not necessary to assume the isotopic composition of the common Pb [14]. Fig. 2 shows the linear regression for the total U/Pb isochron projected onto the $^{238}U/^{206}Pb$-$^{207}Pb/^{206}Pb$ plane.

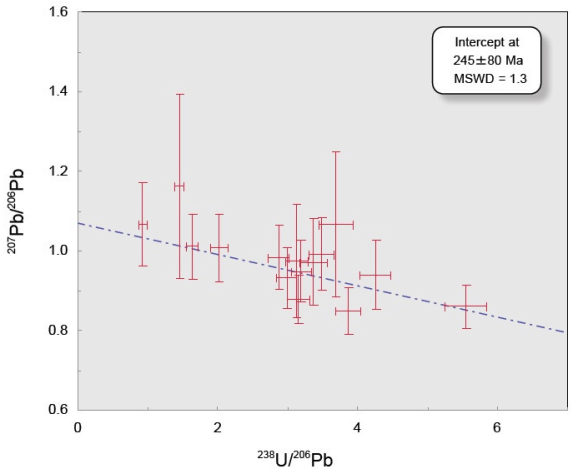

Fig. 2. The result of 3-D linear regression of phosphates in Zagami, projected onto $^{238}U/^{206}Pb$-$^{207}Pb/^{206}Pb$ diagram. Uncertainties are potrayed at the 2σ level.

A total Pb/U isochron age is estimated by 245±80 Ma (95% CL; MSWD=1.3), consistent with the first TIMS age of 230±5 Ma [5], but apparently older than the second TIMS age of 156±6 Ma [8] and baddeleyite U-Pb age of 183±7 Ma [10]. We have calculated total Pb/U isochron ages of phosphate data by IMS-1280 [10] and SHRIMP [7], where the former age becomes 122±140 Ma (95% CL; MSWD=0.72) and the latter 300±84 Ma (95% CL; MSWD=2.7). When we take into account the weighted average of error of three independent SIMS data [7,10 and this work], U-Pb system of Zagami phosphates yields a formation age of 249±54 Ma. Again this age is consistent with the whole rock U-Pb age [5], but older than residue [8] and baddeleyite ages [10]. This suggests that Zagami phosphates may keep older geochemical signature than those of minerals more resistant to chemical alteration.

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