INITIAL 244PU/238U RATIOS AND SEARCH FOR PRESOLAR SIC IN CAIS INFERRED FROM NOBLE GAS AND TRACE ELEMENT ABUNDANCES IN CAIS FROM CV3 CHONDRITES. D. Nakashima[1], J. M. Friedrich[2], and U. Ott[3,4]. [1]Tohoku University, Sendai 980-8578, Japan (dnaka@tohoku.ac.jp), [2]Fordham University, NY 10458, USA. [3]Max-Planck Institute for Chemistry, 55128 Mainz, Germany. [4] MTA Atomki, 4026 Debrecen, Hungary.

Introduction: Ca-Al-rich inclusions (CAIs) are the oldest solar system solids (~ 4567-4568 Ma; e.g., [1]). The very ancient formation ages allow expecting the presence of isotope anomalies resulting from the decay of short-lived extinct nuclides; e.g., Xe isotope anomalies by ^{244}Pu fission. Plutonium and uranium are both actinides and are therefore products of r-process nucleosynthesis. Pu-244 is a short-lived nuclide with a half-life of ~ 80 Myr and ^{238}U is a long-lived nuclide with a half-life of ~ 4.47 Gyr, so that the ^{244}Pu/^{238}U ratio changes with time and is important as a chronometer for the time interval between the termination of the last contributing r-process nucleosynthesis event and the formation of the solar system (~ 100 Ma; e.g., [2]). It has been proposed that the ^{244}Pu/^{238}U ratio at the solar system formation, $(^{244}Pu/^{238}U)_0$, is 0.0068 ± 0.0010 from an equilibrated ordinary chondrite [3]. The proposed ratio seems to represent the solar system $(^{244}Pu/^{238}U)_0$ ratio, as other solar system materials such as achondrites, chondrules, and terrestrial zircon have similar $(^{244}Pu/^{238}U)_0$ ratios [4 and references therein]. However, CAIs from the Allende CV3 chondrite have distinct $(^{244}Pu/^{238}U)_0$ ratios with an average of 0.087 ± 0.011, which is interpreted as a result of Pu-U fractionation during CAI formation [5].

Curious Marie is a fine-grained CAI, characterized by a group II REE pattern and extremely high Nd/U ratio [6]. Pravdivtseva et al. [7] observed excesses of ^{130}Xe and ^{86}Kr in the CAI and interpreted this as the result of incorporation of presolar SiC into the CAI. One might expect that other CAIs also contain presolar SiC.

In this study, we analyzed noble gas and trace element abundances in five CAIs from CV3 chondrites to see if (1) the Pu-U fractionation caused the high $(^{244}Pu/^{238}U)_0$ ratios in CAIs and (2) the CAIs show noble gas isotope anomalies due to presolar SiC.

Analytical Methods: Five CAIs were handpicked from two CV3 chondrites, Allende and Axtell. Adhering dark matrix material was removed with a dental pick and a tweezer. The five CAIs were separated into two pieces respectively for analyses of noble gas isotopes (25.3 – 136 mg) and trace element abundances (31.4 – 154 mg). Isotope ratios and concentrations of noble gases in the five CAIs were measured by stepwise heat-ing from 600 to 1800 °C with 200 °C intervals using the MAP215-50 noble gas mass spectrometer at MPI-Mainz. The abundances of rare earth elements (REEs), Th, and U were measured with a double-focusing Nu Plasma MC-ICPMS at MPI-Mainz.

Results and discussion: Noble gas isotope ratios of the five CAIs indicate that they are mixtures of fission, spallogenic, neutron-induced, radiogenic, and trapped noble gases. The trapped component may be derived from the adhering dark matrix. Ne isotope ratios scatter around spallogenic Ne with ^{21}Ne/^{22}Ne ratios of 0.7 – 0.9, which are higher than those of *Curious Marie* (0.6 – 0.7; [7]). The low ^{21}Ne/^{22}Ne ratios of *Curious Marie* are explained by a major contribution of spallogenic Ne from Na contained in nepheline and sodalite, secondary alteration products [7]. The higher ^{21}Ne/^{22}Ne ratios of our five CAIs suggest that these CAIs were less affected by secondary alteration, which is supported by the ^{38}Ar/^{36}Ar ratios. Only the 800 °C fraction of one of our CAIs shows a ^{38}Ar/^{36}Ar ratio (0.125), which is lower than that of trapped Ar (0.188), which implies a contribution of Ar from the Cl (n,γ) Ar reaction in sodalite (ratio of 0.003 [8]). The ^{38}Ar/^{36}Ar ratios for the totals of the five CAIs are within the range from 0.188 to 1.54 (spallogenic Ar; [9]).

The REE abundances of the five CAIs are variable from ~ 3 x CI to 20 x CI. Three out of the five CAIs show flat REE patterns (group V). Other two show depletions of Eu and Yb (group III). The U concentrations of the five CAIs range from 14 to 47 ppb.

^{244}Pu/^{238}U ratios: The concentrations of ^{244}Pu-derived ^{136}Xe are calculated as from 1.6 x 10^{-12} to 2.7 x 10^{-11} cc/g. Since Nd is geochemically similar to Pu [10], the Nd/U ratios are used as a proxy for the Pu-U fractionation. As shown in Fig. 1, the initial ^{244}Pu/^{238}U ratios at 4.56 Ga, $(^{244}Pu/^{238}U)_0$, of the five CAIs range from 0.010 to 0.064, correlating with the $(Nd/^{238}U)_0$ ratios. Considering that U is more volatile than Pu and Nd [10], the high $(^{244}Pu/^{238}U)_0$ ratios probably reflect Pu-U fractionation during the CAI formation, as suggested in [5]. The value at the intersection of the correlation line and horizontal line - representing the $(Nd/^{238}U)_0$ ratio in the early solar system of 44.6 [11] - corresponds to the $(^{244}Pu/^{238}U)_0$ ratios before Pu-U fractionation in the CAI formation region and is estimated as 0.0090 ± 0.0032 (2σ). The estimated value is consistent with the inferred solar system $(^{244}Pu/^{238}U)_0$ ratio of 0.0068 [3] within the uncertainty. It is therefore suggested that the $(^{244}Pu/^{238}U)_0$ ratios were homogeneous at least in the inner part of the early solar system. *Curious Marie*, which has an extremely high Nd/^{238}U ratio [6], shows higher (^{244}Pu/^{238}U)$_0$ ratio of 4.88 than the five CAIs, though the data point plots below the regression line (Fig. 1).

Presolar SiC: Fig. 2 shows a Xe three-isotope diagram for ^{130}Xe, ^{131}Xe, and ^{132}Xe after correction for fission Xe. The data for our five CAIs fall along a mixing line defined by spallogenic Xe and Q-Xe [12-13], without evidence for an ^{130}Xe excess. This differs from the case of *Curious Marie*, which exhibits an excess of ^{130}Xe relative to the mixing line, which is attributed to the presence of presolar SiC [7]. In earlier studies of other fine-grained CAIs, which had been irradiated with neutrons, small and variable excesses of ^{130}Xe had been observed [14], therefore, Pravdivtseva et al. [7] suggested that presolar SiC was generally present in the CAI forming region and survived high temperature processes during CAI formation. Given the lack of evidence for presolar SiC in the five CAIs analyzed in this study, it appears that either not all CAIs acquired discernible amounts of presolar SiC, or that not all CAIs were able to preserve presolar SiC during CAI formation. We have also re-analyzed the results of [8], and in their fine-grained CAIs, find evidence for presence (and absence) of Xe-G (not plotted in Fig. 2). Their CAIs, like *Curious Marie*, contain significantly larger excesses of ^{129}I-derived ^{129}Xe than ours, with a roughly similar ^{130}Xe-G/^{129}Xe* ratio. While not discussed in [7], the same (constant) ratio is also seen in the stepwise degassing data for *Curious Marie*. This may suggest a, rather puzzling, coupled occurrence (or absence). In summary, we may be able to say that being fine-grained is not the requirement for having presolar SiC. Coordinated study between mineralogy and noble gas analysis of CAIs may give a clue to understanding what causes the presence in or absence from CAIs of presolar SiC.

References: [1] Connelly J.N. et al. (2012) *Science, 338,* 651-655. [2] Lugaro M. et al. (2014) *Science, 345,* 650-653. [3] Hudson G.B. et al. (1989) *Proc. 19th Lunar and Planetary Science Conference,* pp. 547-557. [4] Nakashima D. et al. (2018) *M&PS, 53,* 952-972. [5] Podosek F.A. and Lewis R.S. (1972) *EPSL, 15,* 101-109. [6] Tissot F.L.H. et al. (2016) *Sci. Adv, 2,* e1501400. [7] Pravdivtseva O. et al. (2020) *Nat. Astron., 4,* 617-624. [8] Göbel R. et al. (1982) *GCA, 46,* 1777-1792. [9] Wieler R. et al. (2002) *RMG, 47,* 125-170. [10] Boynton W.V. et al. (1978) *EPSL, 40,* 63-70. [11] Lodders K. (2003) *ApJ, 591,* 1220-1247. [12] Hohenberg C.M. et al. (1981) *GCA, 45,* 1909-1915. [13] Busemann H. et al. (2000) *M&PS, 35,* 949-973. [14] Pravdivtseva O. et al. (2003) *GCA, 37,* 5011-5026.

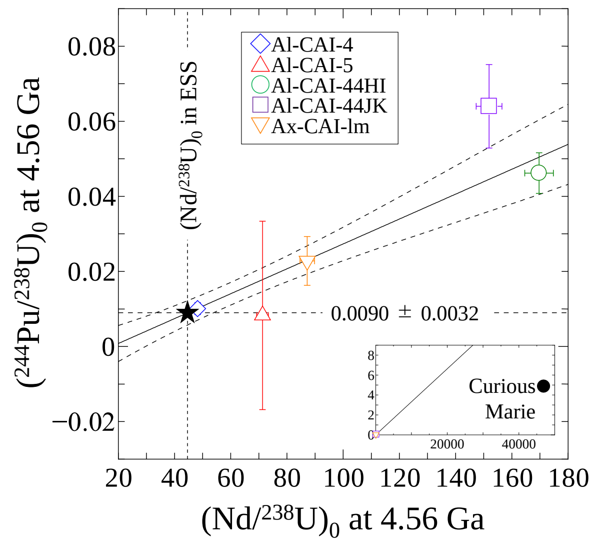

Fig. 1: Correlation between initial (^{244}Pu/^{238}U)$_0$ and (Nd/^{238}U)$_0$ ratios for the five CAIs of this study. The solid line represents the correlation line with the curved lines giving the 2σ confidence interval. The value at the initial (Nd/^{238}U)$_0$ ratio in the early solar system (ESS; vertical dashed line) of 0.0090 ± 0.0032 (dashed horizontal line) defines the CAI value before Pu-U fractionation. The values for Curious Marie are plotted in the insert for comparison [6-7].

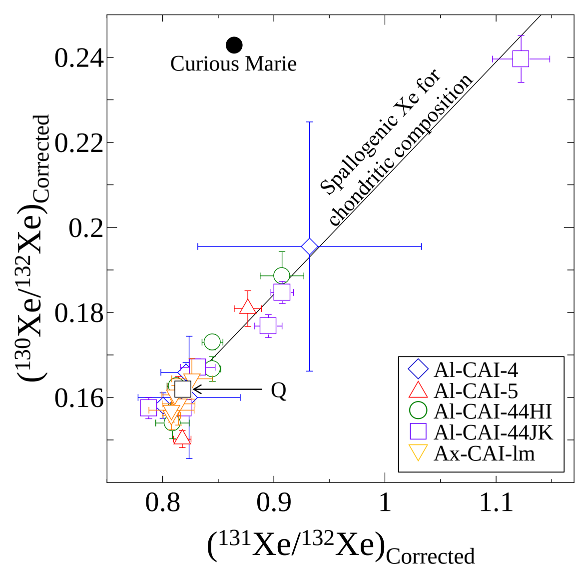

Fig. 2: Xe three-isotope diagram for ^{130}Xe, ^{131}Xe, and ^{132}Xe corrected for fission Xe. The data for Curious Marie [7] are plotted for comparison.