

**I-Xe STUDIES OF AQUEOUS ALTERATION IN THE ALLENDE CAI CURIOSUS MARIE.** O. Pravdivtseva<sup>1</sup>, A. Meshik<sup>1</sup>, F. L. H. Tissot<sup>2</sup>, N. Dauphas<sup>3</sup>. <sup>1</sup>Laboratory for Space Sciences and Physics Department, Washington University, CB1105, One Brookings Drive, Saint Louis, MO 63130 ([olga@physics.wustl.edu](mailto:olga@physics.wustl.edu)), <sup>2</sup>Department of the Earth, Atmospheric and Planetary Sciences, MIT, Cambridge 02139, <sup>3</sup>Origins Lab, The University of Chicago.

**Introduction:** The Allende fine-grained inclusion *Curious Marie* is a unique CAI. It is depleted in uranium but contains large <sup>235</sup>U excess [1], providing new evidence that <sup>247</sup>Cm was alive in the Early Solar System, as has been previously suggested [2], and leading to an updated (<sup>247</sup>Cm/<sup>235</sup>U)<sub>initial</sub> ratio of  $(1.1 \pm 0.3) \times 10^{-4}$ .

A model initial <sup>26</sup>Al/<sup>27</sup>Al ratio  $[(6.2 \pm 0.9) \times 10^{-5}]$  has been calculated for *Curious Marie* using its bulk Al/Mg ratio and the uniform  $\delta^{26}\text{Mg}^* \sim +4\text{‰}$  [3] which is similar to the canonical initial solar system value within error. This implies not only an early condensation of the CAI precursor, but also an early onset for the aqueous alteration as well. If this episode of aqueous alteration was responsible for the depletion of U in *Curious Marie*, the initial solar system value for <sup>247</sup>Cm/<sup>235</sup>U ratio is  $(5.6 \pm 0.3) \times 10^{-5}$  [3].

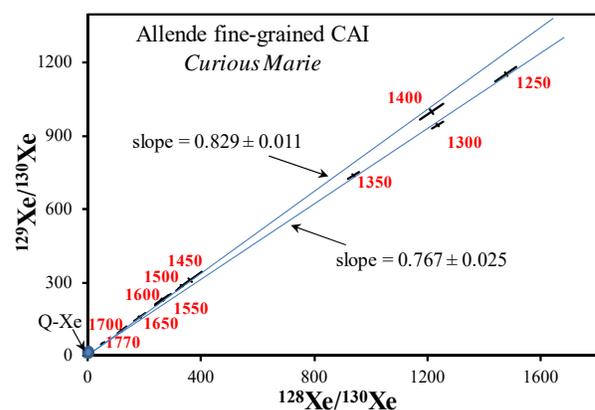
*Curious Marie*, an extremely altered U-depleted fine-grained CAI, characterized by a group II REE pattern with extensive replacement of high-T phases by low-T alteration products such as nepheline and sodalite. I-Xe chronometry for coarse- and fine-grained Allende CAIs have been previously reported [4,5] with I-Xe ages reflecting the time of alteration. To better delineate the aqueous alteration sequence in Allende CAIs we analyzed Ne, Ar, Kr and Xe isotopic compositions in *Curious Marie* CAI. Here we discuss Xe isotopic composition and the I-Xe chronometry for this sample.

**Experimental:** 27.1 mg of *Curious Marie* was extracted using dental tools under a stereoscopic microscope. The sample was split into two aliquots, 6.7 mg and 20.4 mg. The smaller one, together with the Shallowater standard, was irradiated in the Missouri University Research Reactor (MURR), receiving  $\approx 2 \times 10^{19}$  n/cm<sup>2</sup>.

Xe from irradiated *Curious Marie* CAI was released in step-wise heating extractions in the W coil of our resistance furnace starting with 800°C and up to the melting of Pt (1770°C), with 50°C steps in 1100–1700°C interval. The isotopic composition of the released Xe was measured by high transmission ion-counting mass spectrometry [6] with sensitivity for <sup>132</sup>Xe of  $5.88 \times 10^{-16}$  cm<sup>3</sup> STP/count. Unirradiated *Curious Marie* CAI was analyzed following the same step-wise heating protocol, but in that sample, we also measured the isotopic compositions of Ne, Ar and Kr.

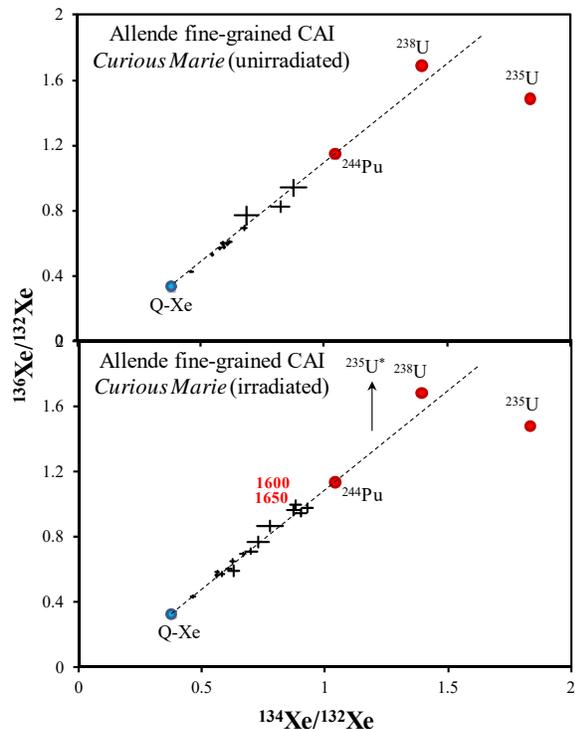
**Results:** Xe in both *Curious Marie* aliquots is dominated by natural radiogenic Xe components. Concentrations of <sup>129</sup>Xe are  $3 \times 10^3$  higher than the trapped <sup>132</sup>Xe, with yet smaller additions of fission Xe. Analyses of the unirradiated *Curious Marie* aliquot revealed <sup>80,82</sup>Kr contributions from natural neutron-capture on <sup>79,81</sup>Br, with <sup>80</sup>Kr/<sup>82</sup>Kr ratio of 2.6, similar to what was previously reported for Allende inclusions [7]. A cosmogenic neutron contribution was also observed as excess <sup>128</sup>Xe. In the unirradiated sample it resulted in a correlation between radiogenic <sup>129</sup>Xe (from <sup>129</sup>I decay) and <sup>128</sup>Xe (from cosmogenic neutron capture). The <sup>129</sup>Xe/<sup>132</sup>Xe versus <sup>128</sup>Xe/<sup>132</sup>Xe isochron for the MURR irradiated sample is  $\sim 1000$  greater than for the naturally irradiated sample. This means *Curious Marie* experienced a thermal equivalent cosmogenic neutron fluence of  $2 \times 10^{16}$  n/cm<sup>2</sup>.

Irradiation in the reactor with the thermal neutrons fluence of  $\approx 2 \times 10^{19}$  n/cm<sup>2</sup> results in the <sup>128</sup>Xe concentrations that are compatible with those for <sup>129</sup>Xe, with typical <sup>129</sup>Xe/<sup>128</sup>Xe ratios that are  $\sim 1$ . So, for the irradiated *Curious Marie* CAI, contribution to <sup>128</sup>Xe from the cosmogenic component constitute only about 0.1% of the total measured <sup>128</sup>Xe, and its effect on the resulting I-Xe age is negligible. Three-isotope plot for the irradiated *Curious Marie* aliquot is shown in Figure 1.



**Figure 1.** Three-isotope plot for the Allende *Curious Marie* CAI. The I-Xe isochrons (free-fit, not forced through Q-Xe) correspond to low- and high-temperature releases of radiogenic Xe.

Apparently, the I-Xe system survived intact in two different mineral phases in *Curious Marie*, contrary to what was previously observed for Allende CAIs [4]. The difference in slopes of the two isochrons corresponds to a difference in closure times of  $1.8 \pm 0.4$  Ma for these two phases (Fig1), independent of other factors. Relative to the Shallowater standard ( $4562.4 \pm 0.2$  Ma [8]), the low- and high-temperature host phases closed  $3.2 \pm 0.7$  Ma and  $1.4 \pm 0.2$  Ma after that standard, corresponding to absolute closure times of  $4559.2 \pm 0.7$  Ma and  $4561.0 \pm 0.2$  Ma.



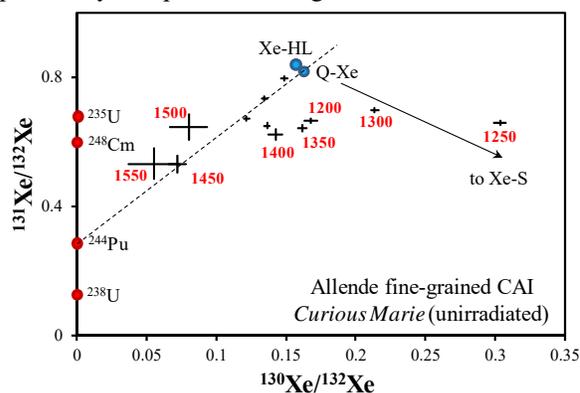
**Figure 2.** The observed fission compositions in the Allende *Curious Marie* aliquots.

The release profiles of fission Xe differed for the irradiated and unirradiated *Curious Marie* samples, suggesting multiple parent isotopes. Likely parents of fission Xe in meteorites are  $^{238}\text{U}$  ( $t_{1/2} = 4.47 \times 10^9$  y),  $^{244}\text{Pu}$  ( $t_{1/2} = 8.0 \times 10^7$  y) and  $^{248}\text{Cm}$  ( $t_{1/2} = 3.4 \times 10^5$  y) [9]. Presence of live  $^{247}\text{Cm}$  at the closure time of the I-Xe system will manifest itself only in the neutron irradiated sample since  $^{247}\text{Cm}$  decays into  $^{235}\text{U}$ . Both samples have major release peaks corresponding to the low-temperature carrier phase. The observed fission composition in this peak for both samples is consistent with Xe from the spontaneous decay of  $^{244}\text{Pu}$ . The release profile of fission  $^{132}\text{Xe}$  for the irradiated *Curious Marie* aliquot also had smaller peak at 1600–1650°C temperature steps (Fig.2), most likely due to neutron-induced fission of  $^{235}\text{U}$ .  $^{136}\text{Xe}$  is always over represent-

ed in the neutron irradiated samples due to neutron capture on live  $^{135}\text{Xe}$  ( $T_{1/2} = 9.10$  h) ( $^{235}\text{U}^*$ , Fig.2).

The observed difference in the release profiles of the irradiated and unirradiated *Curious Marie* samples suggests that U is most likely associated with the high-temperature iodine-carrier phase.

Low-temperature iodine-carrier phase in both *Curious Marie* aliquots demonstrated  $^{130}\text{Xe}$  excesses that were not accompanied by excesses on  $^{124}\text{Xe}$ , expected in case of the spallation contribution (Fig3). We observed similar excess in the same temperature range in one of the previously analyzed fine-grained Allende CAIs [4]. This may well be due to neutron capture on  $^{129}\text{Xe}$ , phenomena observed in the (natural) neutron-irradiated Oklo samples [9]. This is, however, also consistent with Xe component of noble gases carried by pre-solar grains of silicon carbide and points to the possibility that pre-solar SiC grains survived in CAIs.



**Figure 3.** Three-isotope plot for the unirradiated *Curious Marie*.

*Curious Marie* has proven to be an unusual CAI, where two iodine-carrier phases preserved chronological information. Uranium is most likely associated with a high-temperature phase in this sample. If the I-Xe age of this phase of  $4561.0 \pm 0.2$  Ma reflects the time of U loss, the initial  $^{247}\text{Cm}/^{235}\text{U}$  ratio is higher than  $(5.6 \pm 0.3) \times 10^{-5}$ . The  $^{130}\text{Xe}$  excess associated with the low temperature iodine carrier phase suggests that pre-solar SiC may have survived processing of the CAI precursor material.

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**References:** [1] Tissot F.L H. et al. (2016) *LPSC* 47, Abstract#1605. [2] Brennecka G. et al. (2010) *Science* 327, 449–451. [3] Tang et al. (2017) *GCA* 207, 1–18. [3] Swindle T. et al. (1988) *GCA* 52, 2215–2229. [4] Pravdivtseva O. et al. (2003) *GCA* 67, 5011–5026. [5] Hohenberg C. M. (1980) *Rev. Sci. Instrum.* 51, 1075–1082. [6] Göbel R. et al. (1982) *GCA* 46, 1777–1792. [7] Pravdivtseva O. et al. (2017). *GCA* 201, 320–330. [8] Ming T. and Anders E. (1988) *GCA* 52, 1235–1244. [9] Meshik A. et al. (2004) *PRL* 93, 182302-1.