

**MEASURED  $^{238}\text{U}/^{235}\text{U}$  AND A NEW ABSOLUTE AGE FOR THE IVA IRON METEORITE MUONIONALUSTA: A REFINED TIMESCALE FOR PLANETARY EVOLUTION.** G.A. Brennecke<sup>1\*</sup>, T. Kleine<sup>1</sup> <sup>1</sup>Institut für Planetologie, University of Münster, Wilhelm-Klemm-Str. 10, 48149 Münster, Germany, (\*brennecke@wwu.de).

**Introduction:** One major objective of early Solar System chronology is to determine timescales of planetary accretion, differentiation, and cooling. In order to accomplish this, accurate and precise absolute and relative ages from a variety of meteoritic materials are required. Whereas *relative* ages of many keystone events in the early Solar System have been provided by various extinct chronometers, the only chronometer capable of producing *absolute* ages with a precision high enough to distinguish between events occurring in the first few million years is the lead-lead (Pb-Pb) chronometer. When the Pb-Pb chronometer is coupled with a known U isotope ratio, the absolute age of a sample can often be accurately determined with sub-million year precision. However, only a handful of precise absolute ages have been found on meteoritic materials, and only a single precise absolute age is available for an iron meteorite, namely the IVA iron Muonionalusta [1].

Obtaining accurate and precise absolute ages on iron meteorites is particularly important because most iron meteorites are thought to derive from the metal cores of differentiated protoplanetary bodies, and as such, determining the crystallization and cooling timescales of such planetary core material is critical to understanding the early evolution of protoplanets. To date, by far the most ancient and precise cooling age reported for planetary core material comes from troilite inclusions found within the IVA iron meteorite Muonionalusta. The reported Pb-Pb age of  $4565.3 \pm 0.1$  Ma [1] is only ~2 million years younger than CAIs and would, therefore, mandate extremely rapid accretion, differentiation, and cooling of the IVA parent body [1]. Such rapid cooling requires disruption of the IVA parent body and removal of any insulating silicate mantle [2]. Moreover, thermal modeling comparing IVA meteorites suggests that some samples would have cooled contemporaneously with CAI formation [3], which is not only extremely unlikely, but is inconsistent with ages obtained from short-lived chronometers [4].

Prior to ~2010—and including the Pb-Pb chronology of Muonionalusta—the U-isotope value of meteoritic material was simply assumed to be invariant ( $^{238}\text{U}/^{235}\text{U}=137.88$ ). However, this value has since been shown to vary in many Solar System objects, consequently requiring parallel measurement of the sample's  $^{238}\text{U}/^{235}\text{U}$  in the substance being investigated with the Pb-Pb chronometer [e.g., 5-7]. To test the robustness of the previously reported Pb-Pb age for

Muonionalusta, we measured the U isotopic composition of troilite nodules from this meteorite.

**Samples and Methods:** Two large troilite nodules from two different slabs of Muonionalusta were removed from the metal matrix using a diamond saw at the University of Münster. Following liberation from the metal, the troilite samples (Troil-1 & Troil-2), along with a piece of Muonionalusta metal were weighed and then leached for 5 minutes in weak HCl to remove any surface contamination. In order to test the fidelity of both the chemical separation and mass spectrometry, two ~35 g terrestrial pyrites were processed alongside the Muonionalusta samples.

**Chemical purification.** All samples were dissolved in concentrated HCl/HNO<sub>3</sub> and reconstituted in large volumes of 3M HNO<sub>3</sub>, scaling with the sample size. Uranium purification based on the procedure outlined in [6] was performed twice on each sample to isolate U from the sulfide matrix.

Following removal of the meteoritic U, a known amount of U isotopic standard (20 ng CRM-112a – termed “Matrix-112a”) was added to each of the troilite solutions. An identical chemical protocol from each troilite samples was followed for the removal of the U standard from the troilite sample matrix. Pre- and post-chemistry analyses showed ~95-105% ( $\pm 10\%$ ) of Matrix-112a were recovered from each troilite sample.

Sample	Mass (g)	# of Columns	[U] ppt	pg U
Troilite-1	6.63	6	60	400
Troilite-2	38.75	13	10	390
Muon Metal	10.98	6	<2	<22

**Table 1** – Masses and U contents of samples from this study, along with the number of columns used for chemical separation.

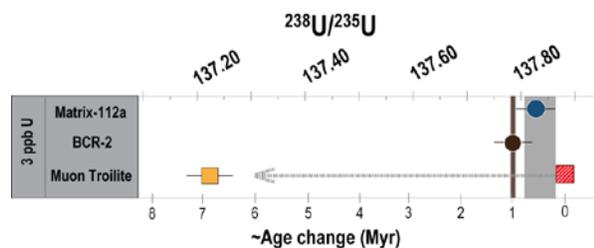
**Mass spectrometry.** Standards were run at both 20 ppb U as well as 3 ppb U to match the same measurement conditions as the samples. The running standard CRM-112a has a determined  $^{238}\text{U}/^{235}\text{U}=137.837 \pm 0.015$  [9] and was measured at various concentrations throughout the campaign to monitor and correct for instrumental drift. The reported uncertainty is calculated as  $2 \times$  the standard deviation of multiple runs (2SD). Similar to many previous works, samples were spiked following chemical separation with an appropriate amount of  $^{233}\text{U}$ - $^{236}\text{U}$  double spike to correct for mass bias during the measurements [5, 7-8, 10-11].

**Isotopic results.** The reproducibility of CRM-112a was  $\pm 0.010$  when measured at 20 ppb U, and  $\pm 0.029$

when measured at 3 ppb U. The basalt standard BCR-2 measured at both concentrations (20 ppb and 3 ppb) was indistinguishable from previous work reporting on the same geologic standard [7, 10]. The  $^{238}\text{U}/^{235}\text{U}$  of the terrestrial pyrite samples were determined to be  $137.707\pm 0.010$  and  $137.731\pm 0.010$ , respectively. These values are entirely consistent with previously investigated U isotopes from terrestrial ore deposits [9-10]. The measured  $^{238}\text{U}/^{235}\text{U}$  of Matrix-112a was indistinguishable from the unprocessed standard for both 20 ppb and 3 ppb concentrations.

These tests provide confidence that 1) the chemical separation method chosen to remove U from a large sulfide matrix does not induce analytical artifacts, and 2) the chosen measurement procedure using only 250  $\mu\text{L}$  of solution at 3 ppb U does not affect the accuracy of the measurement, but simply increases the uncertainty due to the lower amount of total U.

Due to the extremely low U contents of both troilite samples, Troilite-1 and Troilite-2 were combined following U removal to obtain enough U for a single measurement of the  $^{238}\text{U}/^{235}\text{U}$  ratio. For Muonionalusta troilite, we report a  $^{238}\text{U}/^{235}\text{U}$  value of  $137.223\pm 0.045$ . The reported uncertainty includes measurement uncertainty, uncertainty associated with blank subtraction, as well as uncertainty associated with the absolute value of the CRM-112a standard [9], where all individual sources of uncertainty are combined quadratically. Relevant samples and standards are shown in Figure 1, all measured under the same conditions.



**Figure 1** – The  $^{238}\text{U}/^{235}\text{U}$  of Muonionalusta troilite and the associated standards run with the same operating conditions. The grey bar on the right represents the value and long-term reproducibility of CRM-112a run at 3 ppb U. The brown bar represents the previously determined value of BCR-2 run at ideal conditions [7]. The previously assumed  $^{238}\text{U}/^{235}\text{U}$  [1] is displayed with the red hatched box. The yellow box represents the measured value. The accompanying age correction for Muonionalusta is given at the bottom.

**Discussion:** *Origin of  $^{235}\text{U}$  enrichment?* Previous work has shown that the decay of  $^{247}\text{Cm}$  in the early Solar System is a likely cause for  $^{235}\text{U}$  enrichment in refractory inclusions [5]. However, based on measured Nd/U and Th/U ratios in the troilite samples,  $^{247}\text{Cm}$  decay cannot be the cause of the relative  $^{235}\text{U}$  excess in Muonionalusta unless Nd and Th are not at all representative proxies for the behavior of Cm during metal-silicate and metal-sulfide segregation.

One potential explanation for the relative enrichment of  $^{235}\text{U}$  in Muonionalusta is U-isotope fractionation during core formation. Uranium is *extremely* depleted in planetary core materials, such as Muonionalusta (appropriate  $D_{\text{U}}^{\text{sulfide/silicate}} = 0.00002$ , as determined by [13]). If isotope fractionation occurs during metal-silicate segregation, the degree of fractionation could be high in the non-silicate (core) portion. This scenario requires continuous exchange of U between the silicate and metal-sulfide liquid during movement within the planetoid, in which the light isotope is enriched in the metal portion. This direction of fractionation is similar to Si and Mo [14-15]; however, no experimental data are available for U-isotope fractionation during metal-silicate segregation.

**Implications:** Using a measured  $^{238}\text{U}/^{235}\text{U}$  of  $137.223\pm 0.045$  and Pb data from [1], we report a revised Pb-Pb age for Muonionalusta troilite of  $4558.4\pm 0.5$  Ma. This new age provides  $\sim 8$  to 9 million years for the core of the IVA parent body to cool to the Pb-Pb closure temperature,  $\sim 7$  million years more than previously reported [1]. This substantial adjustment to the cooling period has major implications for models of protoplanetary formation and evolution. Additionally, protracted cooling of the IVA core results in a much slower cooling rate ( $\sim 150^\circ\text{C}/\text{Ma}$ ) for Muonionalusta, and no longer requires an early breakup of the IVA parent body to explain the previously reported ancient Pb-Pb age.

Moreover, a revised Pb-Pb age resolves the lack of significant  $^{60}\text{Fe}$  in Muonionalusta, as reported by [14], and furthermore establishes Muonionalusta an ideal “anchor” meteorite for the short-lived  $^{107}\text{Pd}$ - $^{107}\text{Ag}$  system. This revised age, paired with recent Pd-Ag isotopic data from Muonionalusta [17] and the CAI age of [6], establishes a Solar System initial  $^{107}\text{Pd}/^{108}\text{Pd} = 6.6\pm 0.4\times 10^{-5}$ . This value is in agreement with, but significantly more precise than the value reported by [18].

**References:** [1] Blichert-Toft et al. (2010) *EPSL* 296, 469. [2] Yang et al. (2007) *Nature* 446, 888. [3] Moskovitz & Walker (2011) *EPSL* 308, 410. [4] Kruijer et al. (2014) *Science* 344, 1150. [5] Brennecka et al. (2010) *Science* 327, 449. [6] Connelly et al. (2012) *Science* 338, 651. [7] Goldmann et al. (2015) *GCA* 148, 145. [8] Weyer et al. (2008) *GCA* 72, 345. [9] Richter et al. (2010) *IJMS* 295, 94. [10] Brennecka et al. (2015) *MAPS* 50, 1995. [11] Brennecka et al. (2010) *EPSL* 291, 228. [12] Murphy et al. (2014) *EPSL* 388, 306. [13] Wheeler et al. (2006) *GCA* 70, 1537. [14] Shahar et al. (2011) *GCA* 75, 7688. [15] Hin et al. (2013) *EPSL* 379, 38. [16] Moynier et al. *ApJ* 741, 71. [17] Matthes et al. *this meeting*. [18] Schönbachler et al. (2008) *GCA* 72, 5330.