IMPROVED PRECISION FOR AL-MG CHRONOLOGY OF CHONDRULES HAVING MESOSTASIS WITH MEDIUM MG CONTENT (0.5-1 WT%). G. Siron[1], K. Fukuda[1], and N.T. Kita[1]. [1]WiscSIMS, University of Wisconsin-Madison, Madison, WI 53706, USA (siron@wisc.edu).

Introduction: The ^{26}Al-^{26}Mg chronometer has been a powerful tool to determine relative ages of early Solar System solids precisely due to its short half-life ($\tau_{1/2}$ =0.705 Ma) [1]. In ferromagnesian chondrules, excess ^{26}Mg is generally limited to a few‰ or less due to low abundance of Al-bearing minerals and lower initial (^{26}Al/^{27}Al)$_0$ (<10^{-5}). An earlier study by [2] analyzed chondrules in unequilibrated ordinary chondrites (UOCs) using single electron multiplier (EM) with small primary beam sizes (3-5 µm) targeting mesostasis with relatively high ^{27}Al/^{24}Mg ratio (30-100) and found a short duration of their formation ages (<1 Ma). Recent studies by [3-4] analyzed similar UOC chondrules using multi-collector Faraday cups (MCFC) with large primary beams (30-40 µm), mainly on glassy mesostasis (lower ^{27}Al/^{24}Mg ≤10), and indicate a longer duration (~1.5 Ma).

Recent analytical development for WiscSIMS IMS 1280 allowed us to obtain high precision Al-Mg analyses using smaller primary beam on plagioclase with extremely high ^{27}Al/^{24}Mg ratio (200-2000) [5-6]. Here we present new methods to analyze plagioclase and glassy mesostasis with moderate ^{27}Al/^{24}Mg (30-70) that typically show limited excess in δ^{26}Mg*. We explored two different analytical conditions using a small spot size (~6 µm) and a medium spot size (~15 µm). Additionally, the potential matrix effect on δ^{26}Mg* measurements of olivine and pyroxene were evaluated using 18 mineral standards of different composition. Application to unequilibrated ordinary chondrites (UOCs) of low subtypes (3.01-3.05) is presented in this meeting [7].

SIMS Methods: Primary O_2^- beam was focused in Gaussian mode and obtained 0.17 nA for ~6 µm and 4 nA for ~15 µm beam sizes. In both cases, secondary intensities of ^{24}Mg$^+$ (~5×10^5, ~10^7 cps) and ^{27}Al$^+$ (2×10^7, 4×10^8 cps) were strong enough for FC with the feedback resistors of 10^{12} Ω and 10^{11} Ω, respectively. Minor isotopes ^{25}Mg$^+$ and ^{26}Mg$^+$ were measured using EMs for small spot size (referred as FC-EM), while they were measured on FCs (10^{12} Ω) for medium spot size (referred as MCFC) analyses. Olivine and pyroxene were measured using 1 nA and 8 µm spot size (^{24}Mg$^+$ ~2×10^8 cps) under the MCFC using 10^{11} Ω feedback resistors [5].

We define Δ^{26}Mg$_m$ as mass fractionation corrected raw-measured ratio by using power function with the coefficient β according to the formulation in [8]. The β is assigned to be 0.5128 [9] except for olivine and pyroxene analyses. The Δ^{26}Mg$_m$ values of standards in the same analysis session are used to estimate excess δ^{26}Mg* in unknown samples [8]. Because of limited range of natural mass fractionation in chondrules, a single value of β is used to correct both natural and instrumental mass dependent fractionation [10].

FC-EM Analysis: A single analysis took 32 min, that include 1600 s (4 s × 400 cycles) integration of three Mg isotopes and ^{27}Al. High voltage (HV) of each EM was adjusted at the 20th and 220th cycles using Cameca software routine. The relative gains of two EM may change during a single analysis, therefore, they were each monitored by a second discriminator and corrected following the method described in [6]. Two anorthitic glass standards (MgO 0.5% and 1% [11]) were used to correct for instrumental bias of Mg isotope ratios and relative sensitivity factor (RSF) for ^{27}Al/^{24}Mg ratios. Internal errors were typically 0.4-0.6‰ (2SE) for Δ^{26}Mg$_m$ and 0.5-1% for ^{27}Al/^{24}Mg ratios. For one of the two analyses sessions for UOC chondrules [7], we observed a drift of Δ^{26}Mg$_m$ over time for the standards, which was corrected using a weighted least square algorithm for each day of analysis (Fig. 1). The p-values for all coefficients were checked to determined which was the best polynomial order to use for drift correction. Reproducibility for standard analyses were typically 0.4-0.7‰ (2SD) for Δ^{26}Mg$_m$, after drift correction.

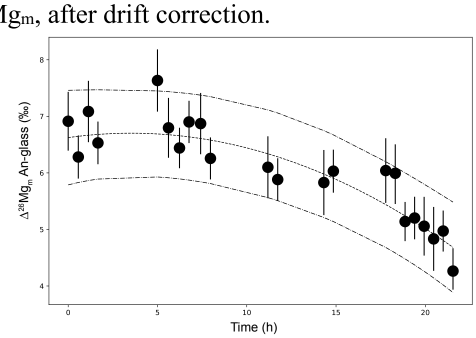

Fig. 1. Example of drift correction of Δ^{26}Mg$_m$ for FC-EM analyses of anorthite.

MCFC analysis of anorthite: We conducted a single MCFC session for the analyses of selected UOC chondrules with large plagioclase [7]. A single analysis takes ~ 8 min including 300 s integrations, which is the same as olivine and pyroxene analyses. The same anorthite glass standards were used to correct for instrumental bias for unknown anorthite. Internal errors of Δ^{26}Mg$_m$ were typically 0.2-0.45‰ (2SE) and reproducibility for the 34 standard measurements of the session was 0.37‰ (2SD). We observed a small linear drift of $\Delta^{26}Mg_m$ for standard (0.4‰ over 6 hours) that was corrected. The internal and external errors for $^{27}Al/^{24}Mg$ were 0.15-0.2% (2SE) and 0.25% (2SD, n=34), respectively.

Olivine and pyroxene analyses: 13 different olivine standards (Fo_{73}-Fo_{100}) and 5 pyroxene standards (two diopside and three low-Ca pyroxenes with Mg# 0.85-0.96) [12] were measured to correct for instrumental bias. Only olivine standards were used to compute the exponent β for the SIMS instrumental mass fractionation ($\delta^{25}Mg_m$ from –4‰ to -1‰). Its value is 0.5169. Using this β, $\Delta^{26}Mg_m$ among olivine standards exhibited a small offset relative to San Carlos olivine standard (Fo_{89}), with a mean value of 0.019 ± 0.047‰ (2SD, n=13). There are significantly large positive offset of 0.150 ± 0.069‰ (2SD, n=3) for $\Delta^{26}Mg_m$ of low-Ca pyroxene standards. Internal errors (2SE) for $\Delta^{26}Mg_m$ were typically 0.04-0.07‰ for olivine and 0.06-0.15‰ for pyroxene. Reproducibility of $\Delta^{26}Mg_m$ from San Carlos olivine standard was typically 0.05‰ (2SD) after linear drift correction.

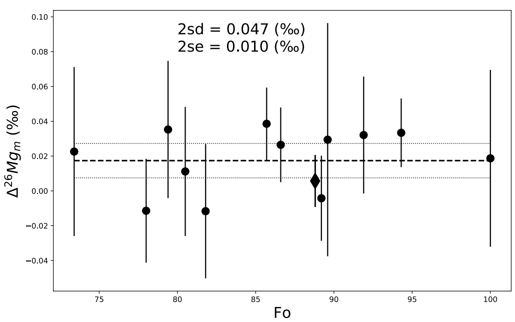

Fig 2. $\Delta^{26}Mg_m$ offset of olivine standards relative to San Carlos olivine standard (black diamond). Error bars represent 2SE of four analyses.

Data reduction of unknowns: Some unknown analyses during FC-EM session penetrated a high-Ca pyroxene next to anorthite grains and were stopped before the end of the 400 cycles. For those analyses, only the cycles from anorthite were taken and standard analyses used for calibrating $\Delta^{26}Mg_m$ were also reduced to the same number of cycles in order to account for the change in $^{27}Al/^{24}Mg$ and possible systematic bias in $\Delta^{26}Mg_m$ with the depth of analyses. Final error for $\delta^{26}Mg^*$ represent the propagation of internal error (2SE), error on the fit for drift correction at the time of the analysis (95% confidence interval) and 2SE of standard measurements. This uncertainty is dominated by the internal error. Uncertainty for $^{27}Al/^{24}Mg$ represent the propagation of internal error (2SE) and 2SE of the standard measurements.

Comparison between MCFC and FCEM: Among 14 chondrules presented in [7], 2 chondrules allowed us to compute two isochrons from MCFC and FC-EM analyses independently. Semarkona c34 (Fig. 3a) exhibit an age after CAI of 1.87 ± 0.07 Ma (FC-EM) and 1.88 ± 0.06 Ma (MCFC). NWA8276 c88 (Fig. 3b) exhibit an age after CAI of 1.83 ± 0.05 Ma (FC-EM) and 1.79 ± 0.04 Ma (MCFC). The results of the two methods for both chondrules are in good agreements within uncertainty and ensure the reliability of new analytical methods.

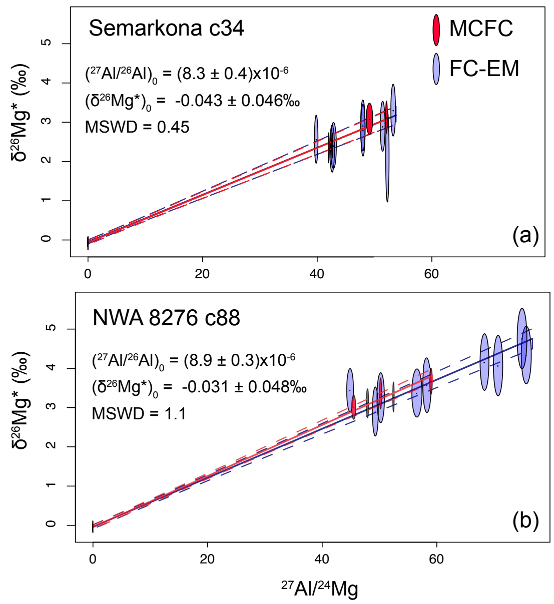

Fig. 3. Isochrons for 2 chondrules that were analyzed by MCFC and FC-EM modes.

Summary: The newly developed method allow for precise measurements (0.05-0.15 Ma) for chondrules having mesostasis with $^{27}Al/^{24}Mg$ of 30-70 and MgO contents of 0.5-1%. The small spot size for FC-EM measurements with a significantly reduced analysis time (3-8 hours vs 30 min) allow to find at least 5-6 areas in many chondrules that were previously very difficult to conduct [e.g., 12]. A small but resolvable deviation of $\Delta^{26}Mg_m$ from a single instrumental fractionation line between olivine and pyroxene standards was observed and properly corrected in this work.

References: [1] Kita N. T. and Ushikubo (2012) *Meteorit. Planet. Sci., 47,* 1108-1119. [2] Kita N. T. et al. (2000) *GCA, 64,* 3913-3922 [3] Villeneuve J. et al. (2009) *Science, 325,* 985-988. [4] Pape J. et al. (2019) *GCA, 244,* 416-436. [5] Hertwig et al. (2019) *GCA, 253,* 111-126. [6] Kita N. T. et al (2019) *LPS L,* Abstract #2213. [7] Siron G. et al. (2020), LPS LI, Abstract #1574. [8] Ushikubo T. et al. (2017) *GCA, 201,* 103-122. [9] Davis A. M. et al. (2015) *GCA, 158,* 245-261. [10] Tenner T. J. et al. (2019) *GCA, 260,* 133-160. [11] Kita N. T. et al. (2012) *GCA, 86,* 37-51. [12] Fukuda K. et al. (2019) *82th Meteoritical Society Meeting,* Abstract #6204.