RELATIVE SENSITIVITY FACTOR DEFINED FOR ^{53}Mn-^{53}Cr CHRONOMETRY OF SECONDARY FAYALITE. P. M. Doyle[1,2*], K. Nagashima[2], K. Jogo[2], and A. N. Krot[1,2]. [1]University of Hawai'i NASA Astrobiology Institute, [2]Hawai'i Institute of Geophysics and Planetology, University of Hawai'i at Mānoa, Honolulu, HI, 96822, USA. *pdoyle@higp.hawaii.edu

Introduction: The iron-rich olivine end-member, fayalite (Fe_2SiO_4), occurs within CV, CO, CK and unequilibrated ordinary chondrites [1]. Although it was proposed that fayalite (*fa*) formed by high temperature nebular processes [2, 3], recent studies favor its formation during low temperature, fluid-assisted alteration in an asteroidal setting [1, 4–6]. As such, the chemical and isotopic composition of *fa* can be used to constrain the temperature of alteration [5, 6], water/rock ratio [6], and O-composition of the fluid [1, 7]. Dating of *fa* formation could provide additional constrains on aqueous activity on asteroids, their structure and thermal history [4, 6, 8].

Fayalite in carbonaceous chondrites contains up to ~2 wt% MnO and <0.03 wt% Cr_2O_3 [2], making it suitable for ^{53}Mn-^{53}Cr dating (^{53}Mn decays to ^{53}Cr with a half-life of 3.7 Ma) using secondary ion mass-spectrometry (SIMS) [4]. A suitable standard is required to determine a relative sensitivity factor (RSF) in order to correct for relative sensitivities between $^{55}Mn^+$ and $^{52}Cr^+$ ions and to calculate ^{55}Mn/^{52}Cr ratios for dating using the isochron method. San Carlos (SC) olivine ($Fa_{\sim10}$) has commonly been used for this purpose [e.g., 4, 6] as, in general, natural fayalite contains only trace amounts of Cr, which makes determining Mn/Cr ratios by electron microprobe (EPMA) very difficult. The relative sensitivity factor, defined as RSF = $(^{55}Mn/^{52}Cr)_{SIMS}/(^{55}Mn/^{52}Cr)_{EPMA}$, from a synthetic glass having a composition of Ca-rich olivine with $Fa_{\sim40}$ was measured to be ~1.6 [9], which is systematically different from the RSFs of ~0.9 and ~0.6 measured on San Carlos olivine by [4] and [6] respectively. If the RSF obtained by [9] is applied to the ^{53}Mn-^{53}Cr data reported for nearly pure fayalite [4, 6], the inferred initial ^{53}Mn/^{55}Mn ratio would become nearly twice higher than the reported values, which would make the relative ^{53}Mn-^{53}Cr ages of *fa* formation ~ 4 Ma older. A homogeneous standard of similar composition to the unknown ($Fa_{>95}$) is therefore needed to obtain accurate ^{53}Mn-^{53}Cr ages for secondary *fa*.

Method: Synthetic olivines with a range of compositions (Fa_{31-100}) were prepared in order to investigate the dependence of the RSF on the fayalite content. For this purpose pre-dried Fe_2O_3, MgO, SiO_2, $MnCO_3$, Cr_2O_3 and NiO were mixed in stoichiometric proportions and ground by hand under ethanol, with five or six repeat grinds per composition. The respective powders were made into a slurry with a polyvinyl alcohol solution and attached to platinum (Pt) loops. The loops were suspended from a Pt chandelier in a 1 atm vertical gas mixing furnace at temperature (1151–1500°C) for up to 20 hours, after which the samples were quenched into water. Mixtures of H_2 and CO_2 were used to control the oxygen fugacity (IW+0.4 to IW+3.2).

Portions of each sample obtained were mounted in epoxy resin, polished and characterized using the JEOL JXA-8500F field emission electron microprobe at the University of Hawai'i (UH). Mn-Cr isotope data were collected from SC olivine, synthetic olivine (Fa_{31-100}) and *fa* in CO/CM MAC 88107 (Fa_{99-100}) using the UH Cameca ims-1280 SIMS. The operating conditions and data reduction protocols are detailed within [8].

Results: Olivine grains in different runs were obtained at sub-solidus temperatures, as liquidus phase from partial melts, and as quenched complete melts (Fig. 1). A few shards of glass having a ferroan olivine stoichiometry (Fa_{96} and Fa_{100}) were recovered, but bulk samples prepared from a molten state had quench skeletal textures (Fig. 1b) which are unsuitable for use as

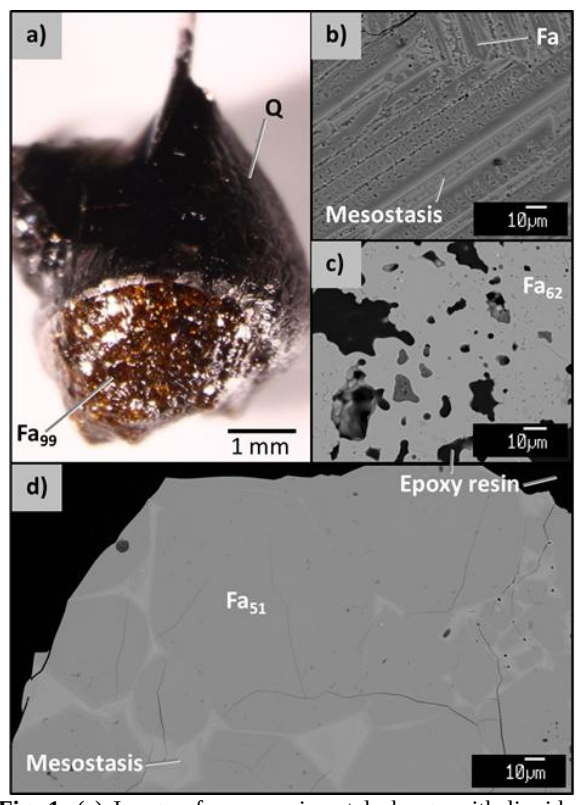


Fig. 1. (a) Image of an experimental charge with liquidus phase *fa* (Fa_{99}) and a mixture of quenched olivine and mesostasis (Q). (b–d) Backscattered electron images of the samples representing (b) quenched olivine and mesostasis, (c) polycrystalline olivine obtained at sub-solidus temperatures, and (d) liquidus olivine grains with mesostasis.

standards. Samples obtained at sub-solidus temperatures have compositions similar to the bulk mixtures ($Fa_{60–100}$). The samples are, however, polycrystalline (Fig. 1c) and heterogeneous in terms of Mn/Cr ratio. In contrast, liquidus olivine grains (Fig. 1d) obtained from partial melts are compositionally homogeneous and sufficiently large to be used as standards for SIMS measurements. The most suitable standards, therefore, are liquidus olivine grains ($Fa_{31–99}$) prepared at IW+1 for ~20 hours. These olivine grains have ~0.8 wt% MnO and ~0.07 wt% of Cr_2O_3, resulting in $^{55}Mn/^{52}Cr$ ratios of ~14.

The Mn-Cr RSF is time-dependent during the measurement, as is observed in carbonates [10], so the RSF was time-averaged. The magnitude of the time-dependence on RSF in SC olivine is different from those in Fa_{31}–Fa_{99}. Furthermore, the RSF increases as a function of fayalite content in olivine from Fa_{10} to ~Fa_{30} and reaches a plateau ~1.4 times higher than the RSF on SC olivine (Fig. 2).

Excess ^{53}Cr in MAC 88107 *fa* is correlated with $^{55}Mn/^{52}Cr$ indicating *in situ* decay of ^{53}Mn (Fig. 3). The isochron defined using a RSF on Fa_{99} has an initial $^{53}Mn/^{55}Mn$ ratio of $(2.45\pm0.33)\times10^{-6}$ (Fig. 3a), equating to 4.6 (+0.8/-0.7) Ma after CV CAIs [8]. The initial $^{53}Mn/^{55}Mn$ ratio of the same dataset reduced using a RSF on SC olivine is $(1.77\pm0.34)\times10^{-6}$ (Fig. 3b), equating to 6.3 (+1.1/-0.9) Ma after CV CAI formation.

Discussion: The inferred initial $^{53}Mn/^{55}Mn$ ratio of $(1.77\pm0.34)\times10^{-6}$ in *fa* from MAC 88107 determined using RSF on SC olivine (Fig. 3b) is consistent with the previously reported value of $(1.58\pm0.26)\times10^{-6}$ [4]. This value, however, differs significantly from the initial $^{53}Mn/^{55}Mn$ ratio of $(2.45\pm0.33)\times10^{-6}$ determined using RSF on Fa_{99}. We infer that the previously published data on $(^{53}Mn/^{55}Mn)_0$ are incorrect and should be discarded. If the Mn-Cr data are corrected with the matrix-matched Fa_{99}, formation of *fa* in MAC 88107 is revised to be ~2 Ma earlier than calculated using a RSF on SC olivine. Indeed, the revised formation age of *fa* in MAC 88107 (4562.7±0.7 Ma) is consistent with the ^{53}Mn-^{53}Cr ages of carbonates in CM chondrites measured using a proper carbonate standard [11].

References: [1] Krot A. N. et al. (2012) *Meteoritics & Planetary Science* 39 (Supp.):5338. [2] Hua X. and Buseck P. (1995) *Geochimica et Cosmochimica Acta* 59:563–578. [3] Weisberg M. K. et al. (1996) *Meteoritics & Planetary Science* 32:791–801. [4] Hutcheon I. D. et al. (1998) *Science* 282:1865–1867. [5] Krot A. N. et al. (2006) *Meteorites and the Early Solar System II*, 525-553. [6] Jogo K. et al. (2009) *Earth and Planetary Science Letters* 287:320–328. [7] Choi B.-G. et al. (2000) *Meteoritics & Planetary Science* 35:1239–1248. [8] Doyle P. et al. (2013) *Lunar and Planetary Science Conference* this issue. [9] Sugiura N. and Miyazaki A. (2006) *Earth, Planets and Space* 58:689–694. [10] Sugiura N. et al. (2010) *Geochemical Journal* 44:11–16. [11] Fujiya W. et al. (2012) *Nature Communications* 3:1–6.

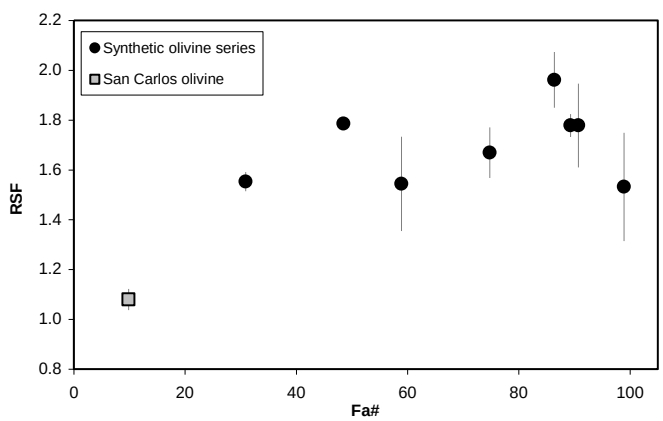
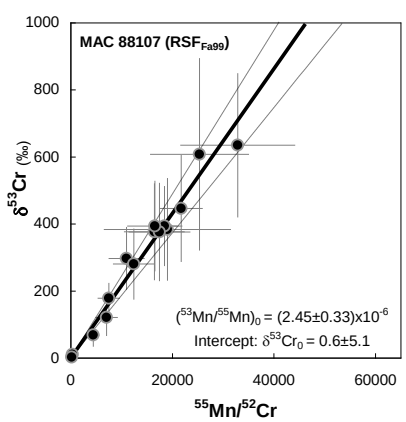


Fig. 2. (left) The relative sensitivity factor [RSF = $(^{55}Mn/^{52}Cr)_{SIMS}/(^{55}Mn/^{52}Cr)_{EPMA}$] as a function of Fa# for SC olivine and a suite of synthetic, liquidus phase olivine grains (2σ standard deviation shown).



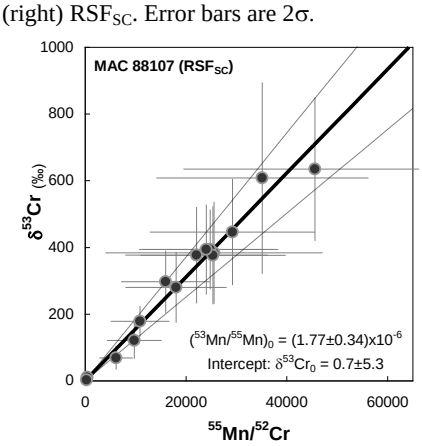


Fig. 3. ^{53}Mn-^{53}Cr evolution diagrams for MAC 88107 fayalite using (left) RSF_{Fa99} and (right) RSF_{SC}. Error bars are 2σ.