

⁶⁰Fe-⁶⁰Ni SYSTEMATICS OF CHONDRULES: CONSTRAINTS FROM *IN SITU* ANALYSES. M. Telus^{1,2}, G. R. Huss², K. Nagashima², R. C. Oglione³, S. Tachibana⁴ ¹DTM, Carnegie Institution of Washington, USA. (mtelus@carnegiescience.edu), ²HIGP, University of Hawai'i at Mānoa, USA. ³Department of Physics, Washington University in St. Louis, USA. ⁴Department of Natural History Sciences, Hokkaido University, Japan.

Introduction: Progress with using the ⁶⁰Fe-⁶⁰Ni ($t_{1/2}=2.6$ Myr) system for early solar system chronology or for constraining astrophysical models has been severely hindered by discrepancies between initial ratios inferred from bulk and *in situ* Fe-Ni analyses. Bulk chondrule analyses imply an initial solar system ⁶⁰Fe/⁵⁶Fe ratio, (⁶⁰Fe/⁵⁶Fe)_{SS}, $<3\times 10^{-8}$ [1], while *in situ* analyses imply initial ratios at least an order of magnitude larger [2-4]. Here, we discuss *in situ* Fe-Ni isotopic data for ferromagnesian silicates in chondrules from unequilibrated ordinary chondrites (UOCs). Although complications from Fe-Ni redistribution make it difficult to interpret the data, our data allow us to place constraints on the upper and lower limits of the initial ⁶⁰Fe/⁵⁶Fe ratio of UOC chondrules.

Samples: We analyzed mainly chondrule pyroxene, but also olivine, from UOCs Semarkona (LL3.00), QUE97008 (L3.05), EET90161 (L3.05), Bishunpur (LL3.1) and Krymka (LL3.2).

SIMS measurements: Chondrules were measured using the University of Hawai'i Cameca ims 1280 ion microprobe. Iron and Ni isotopes were measured as positive ions using a 3-10 nA ¹⁶O⁺ beam. Most analyses were done in multicollection mode [5], though some were in monocollection mode [6]. Spot sizes ranged from 20-40 μm . Molecular interferences on Ni isotopes (*e.g.*, ⁴⁴Ca¹⁶O on ⁶⁰Ni, ⁴⁵Sc¹⁶O on ⁶¹Ni, ⁴⁶Ca¹⁶O on ⁶²Ni) were resolved using a mass resolving power of ~ 4500 (multicollection) or 6000-7000 (monocollection). Interferences were measured during or after each measurement. Terrestrial and synthetic standards were used.

Data analysis: Data were corrected for deadtime, background, drift in the electron multipliers, and tails of interferences. Isotope ratios reported were calculated from total counts to reduce ratio bias [7]. To ensure ratio bias is not an issue, we made sure that ratios normalized to ⁶¹Ni and ⁶²Ni are consistent. Uncertainties on the measured ratios include the standard error of the ratios calculated from individual cycles and uncertainties propagated from standard-sample bracketing.

To calculate ⁶⁰Ni excesses, we applied a linear internal mass-fractionation correction ($\Delta^{60}\text{Ni}=\delta^{60}\text{Ni} + \delta^{62}\text{Ni}$ or $\Delta^{60}\text{Ni}=\delta^{60}\text{Ni} - 2\times\delta^{61}\text{Ni}$) using reference values of 23.0068 and 3.1884 for ⁶⁰Ni/⁶¹Ni and ⁶²Ni/⁶¹Ni, respectively [8]. Relative sensitivity factors were applied to the Fe/Ni ratios. Uncertainties on the Fe/Ni ratios are dominated by the uncertainty on the sensitivity factor and are given as 5% of the measured ratios.

The initial ⁶⁰Fe/⁵⁶Fe ratio for each chondrule is inferred from the error-weighted regression of ⁶⁰Ni/⁶¹Ni (or ⁶⁰Ni/⁶²Ni) vs. ⁵⁶Fe/⁶¹Ni (or ⁵⁶Fe/⁶²Ni). Uncertainties on the isochron slopes, (⁶⁰Fe/⁵⁶Fe)₀, are reported as 2σ . For each isochron, we report the mean square weighted deviation (MSWD), which characterizes goodness of fit to the linear regression. Well-correlated regressions will have MSWDs close to 1.

Results: Initial ⁶⁰Fe/⁵⁶Fe ratios from our chondrule data fall into four main groups: 1) those with large uncertainties due to low Fe/Ni ratios, 2) those with large uncertainties due to insufficient spread in Fe/Ni ratio, 3) those that have unresolved initial ratios despite having high Fe/Ni ratios, and 4) those with resolved initial ratios, but a poor correlation between excess ⁶⁰Ni and the Fe/Ni ratios, yielding large MSWD values.

Initial ratios with uncertainties less than 3×10^{-7} and MSWD values between 0.5 and 1.5 provide the best constraints (Fig. 1, left). These filters allow us to choose chondrule data with well-correlated regressions and relatively small uncertainties. For example, chondrules with large uncertainties due to low Fe/Ni ratios or those with a lack of spread in the Fe/Ni ratios are filtered out, and chondrules with poorly correlated data are also filtered out. With these filters, only one chondrule (from Krymka) has a resolved initial ratio of $(2.2\pm 1.5)\times 10^{-7}$. The others are unresolved from zero (Fig. 1, right).

Constraining the upper limit: Assuming that the initial ratios for all of these chondrules reflect their formation time, and not secondary processing, the Gaussian distribution of the (⁶⁰Fe/⁵⁶Fe)₀ for each chondrule can be summed to give a distribution for the entire data set. The 2σ 1-sided upper limit for the summed distribution is 2.6×10^{-7} , consistent with the resolved initial ratio of $(2.2\pm 1.5)\times 10^{-7}$ for the Krymka chondrule.

Complications from Fe-Ni mobilization: Interpretation of the unresolved initial ratios requires caution. Synchrotron X-ray fluorescence maps presented by [9] show clear evidence of extensive open-system Fe-Ni redistribution along chondrule fractures for all UOCs regardless of petrologic type and regardless of whether fall or find. The redistribution of Fe and Ni can result in lower or higher inferred initial ratios.

For example, Krymka chondrule KRM94 ch1 has high ⁵⁶Fe/⁶²Ni ratios (up to 1×10^6), but the inferred initial ⁶⁰Fe/⁵⁶Fe ratio is $<4\times 10^{-8}$. It has a MSWD value between 0.5 and 1.5 and an uncertainty $<3\times 10^{-7}$, so it is one of our best chondrules (Fig. 1). However, synchro-

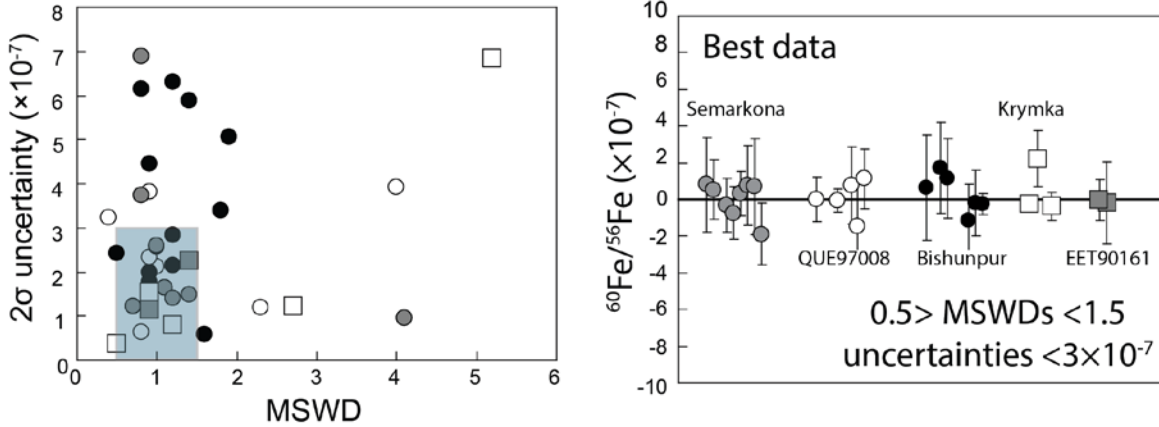


Fig. 1. The 2σ -uncertainty on the initial $^{60}\text{Fe}/^{56}\text{Fe}$ ratios for UOC chondrules vs. MSWD values are plotted on the left. The data for our best chondrules fall in the highlighted area. The initial ratios for those chondrules and their 2σ -uncertainties are shown on the right.

tron XRF maps of this chondrule [10] show extensive Fe-Ni mobilization along the chondrule fractures, with many of our spot analyses overlapping these fine fractures. Since many spot analyses measured extraneous Fe and Ni, the initial ratio inferred from the *in situ* data likely does not reflect its true initial ratio.

Constraining the lower limit: Initial ratios for chondrules that have resolved initial ratios have been disturbed as indicated by the poor correlation between the excesses of ^{60}Ni and the Fe/Ni ratios. Therefore, the inferred initial ratios do not provide reliable constraints on the $(^{60}\text{Fe}/^{56}\text{Fe})_0$ of the chondrules. Since redistribution of Fe and Ni can decrease the $\delta^{60}\text{Ni}$ values, but cannot increase them, observed excesses in ^{60}Ni can be used to place constraints on the lower limit of the $(^{60}\text{Fe}/^{56}\text{Fe})_0$. Assuming the measured $\delta^{60}\text{Ni}$ is the lower limit on the true value and that the highest possible $^{56}\text{Fe}/^{62}\text{Ni}$ ratio for pyroxene is 1×10^7 , then 30% excesses in ^{60}Ni require an initial ratio of at least 5×10^{-8} (Fig. 2). Initial ratios lower than this require Fe/Ni ratios that are unreasonably high.

Conclusions: Given the complications with Fe-Ni redistribution, UOCs may not be appropriate samples for constraining the $(^{60}\text{Fe}/^{56}\text{Fe})_{\text{SS}}$ ratio. Nevertheless, an initial $^{60}\text{Fe}/^{56}\text{Fe}$ ratio for UOCs between 5×10^{-8} and 2.6×10^{-7} can be inferred from our SIMS analyses of chondrules from UOCs. This is an order of magnitude higher than estimates from bulk analyses [1]. The discrepancies between bulk and *in situ* analyses likely stem from complications due to late-stage open-system Fe-Ni mobilization described by [9]. Previously reported *in situ* Fe-Ni systematics of UOC chondrules by [3-4] tend to give higher initial ratios than the best data reported in this study. Since both studies use similar analytical techniques, similar data analyses and similar samples,

the cause of the apparent discrepancy between their analyses and our analyses remains unclear.

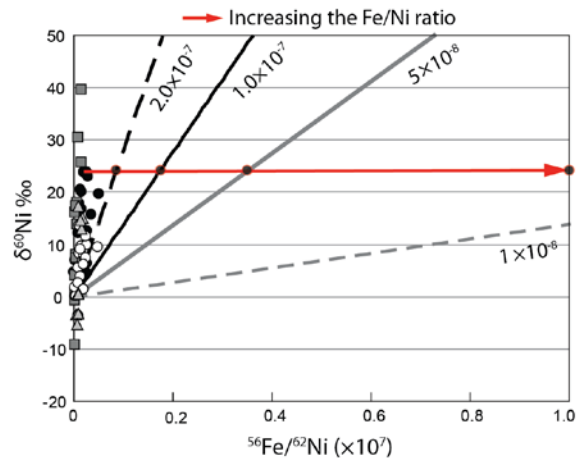


Fig. 2. Fe-Ni SIMS data for chondrules with resolved initial ratios, but large MSWD values. The highest plausible $^{56}\text{Fe}/^{62}\text{Ni}$ ratio for pyroxene is 1×10^7 . Observed excesses in ^{60}Ni of $\sim 30\%$ thus require initial $^{60}\text{Fe}/^{56}\text{Fe}$ ratios of at least 5×10^{-8} .

References: [1] Tang H. and Dauphas N. (2015) *APJ* 802, 1-9. [2] Telus M., et al. (2012) *MAPS* 47, 2013-2030. [3] Mishra R.K. and Chaussidon M. (2014) *EPSL* 398, 90-100. [4] Mishra R.K. and Goswami J.N. (2014) 132, 440-457. [5] Telus M., et al. (2013) *MAPS* 48 (abstract #5294). [6] Telus M., et al. (2011) *LPSC* (abstract #2559). [7] Ogliore R.C., et al. (2011). *NIMB*, 269, 1910-1918. [8] Chen J.H., et al. (2009) *GCA* 73, 1461-1471. [9] Telus M., et al. (2016) *GCA* (accepted). [10] Telus M., et al. (2014) *LPSC* (abstract #2559). Supported by NASA NNX11AN62H (MT) and NNX11AG78G and NNX14AI19G (GRH).