In situ $^{60}\text{Fe}$-$^{60}\text{Ni}$ systematics of chondrules from unequilibrated ordinary chondrites

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Abstract

The initial $^{60}\text{Fe}/^{56}\text{Fe}$ of chondrules from unequilibrated ordinary chondrites (UOCs) can potentially constrain the stellar source of short-lived radionuclides and develop the $^{60}\text{Fe}$-$^{60}\text{Ni}$ ($t_{1/2} = 2.6$ Ma) system for early solar system chronology. However, progress with the $^{60}\text{Fe}$-$^{60}\text{Ni}$ system has been hindered by discrepancies between initial ratios inferred from bulk and in situ Fe-Ni analyses. Telus et al. (2016) show that discrepancies between these different techniques stem from late-stage open-system Fe-Ni mobilization. Here, we report in situ analyses of the Fe-Ni isotopic composition of ferromagnesian silicates in chondrules from UOCs using the ion microprobe. Of the 24 chondrules analyzed for this study, a few chondrules have resolved excesses in $^{60}\text{Ni}$ of up to 70‰; however, the correlations with Fe/Ni are weak. Although complications from Fe-Ni redistribution make it difficult to interpret the data, we show that the initial $^{60}\text{Fe}/^{56}\text{Fe}$ for UOC chondrules is between $5 \times 10^{-8}$ and $3.0 \times 10^{-7}$. This is consistent with a late supernova source for $^{60}\text{Fe}$, but self-enrichment of the molecular cloud is another possible mechanism for incorporating $^{60}\text{Fe}$ in the solar system. Discrepancies between bulk and in situ analyses remain, but likely stem from late-stage open-system Fe-Ni mobilization.

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1. INTRODUCTION

The $^{60}\text{Fe}$-$^{60}\text{Ni}$ short-lived radionuclide system ($t_{1/2} = 2.6$ Ma) has been of interest in cosmochemistry and astrophysics for several reasons, including its potential for constraining early solar system chronology (e.g., Shukolyukov and Lugmair, 1993a; Tang and Dauphas, 2012a), its potential as a heat source for planetary differentiation (e.g., Moskovitz and Gaidos, 2011), identifying the stellar source of short-lived radionuclides (e.g., Huss et al., 2009), and understanding the environmental conditions surrounding the Sun’s formation (e.g., Hester and Desch, 2005). The presence of live $^{60}\text{Fe}$ in the early solar system has been inferred through excesses in $^{60}\text{Ni}$ that correlate with Fe/Ni in various meteorites (e.g., Shukolyukov and Lugmair, 1993a; Tachibana et al., 2006; Tang and Dauphas, 2012a; Mishra and Goswami, 2014). The initial $^{60}\text{Fe}/^{56}\text{Fe}$ for each sample, ($^{60}\text{Fe}/^{56}\text{Fe})_0$, is determined from an evolution diagram, which plots the Ni-isotopic composition as a function of the Fe/Ni. The slope of the correlation line gives ($^{60}\text{Fe}/^{56}\text{Fe})_0$, which can then be used to constrain
the initial solar system $^{60}$Fe/$^{56}$Fe value, $(^{60}$Fe/$^{56}$Fe)$_{BS}$, as long as the age of the sample has been determined independently, the Fe-Ni system has remained closed, and $^{60}$Fe was homogeneously distributed in the solar system. The last two criteria are often assumed.

Progress with using the $^{60}$Fe-$^{60}$Ni system for early solar system chronology or for constraining astrophysical models has been hindered by discrepancies between initial ratios inferred from bulk and in situ Fe-Ni analyses. Bulk Fe-Ni analyses of calcium-aluminum-rich inclusions (CAIs), the first solids to form in the solar system, carried out by Bick and Lugmair (1988), found excesses of $^{60}$Ni in several inclusions consistent with an initial $(^{60}$Fe/$^{56}$Fe)$_{BS}$ of <1.6 x 10$^{-7}$. However, since CAIs preserve Ni-isotope anomalies, it is not clear whether the excesses in $^{60}$Ni are from the decay of $^{60}$Fe or simply inherited isotope anomalies, which are common in CAIs. Further application of CAIs to constrain the $(^{60}$Fe/$^{56}$Fe)$_{BS}$ has been problematic for this reason. Whole rock analyses of eucrites, basaltic achondrites, by Shukolyukov and Lugmair (1993a, 1993b) showed $^{60}$Ni excesses that correlate with Fe/Ni. The initial $(^{60}$Fe/$^{56}$Fe) inferred for eucrites Juvinas and Chervony Kut were 4.3 x 10$^{-10}$ and 3.9 x 10$^{-9}$, respectively, implying an 8.3 Ma difference in the crystallization ages of these meteorites (using the 2.6 Ma half-life determined by Rugel et al., 2009). However, internal isochrons from analyses of mineral separates do not show a tight correlation between excess $^{60}$Ni and Fe/Ni, indicating the Fe-Ni system did not remain closed for these samples and has been affected by thermal metamorphism (Shukolyukov and Lugmair, 1993a; Quité et al., 2011). Whole rock analyses of eucrites and diogenites by Tang and Dauphas (2012a) infer an $(^{60}$Fe/$^{56}$Fe) of 3.5 x 10$^{-9}$ at the end of mantle differentiation of the HED (howardite-eucrite-diogenite) parent body. Using $^{53}$Mn-$^{53}$Cr systematics to infer the time of differentiation, the estimated initial solar system $(^{60}$Fe/$^{56}$Fe) ratio, $(^{60}$Fe/$^{56}$Fe)$_{BS}$, is 1.0 x 10$^{-8}$. This is also consistent with initial ratios inferred from bulk analyses of angrites (Quité et al., 2010; Spivak-Birndorf et al., 2011; Tang and Dauphas, 2012a, 2012b). Bulk analyses of chondrules from unequilibrated ordinary chondrites have also been used to help constrain $(^{60}$Fe/$^{56}$Fe)$_{BS}$. Excesses in $^{60}$Ni are unresolved from zero for most bulk chondrule analyses (Tang and Dauphas, 2012a; Spivak-Birndorf et al., 2012a; Spivak-Birndorf et al., 2012b; Chen et al., 2013); however, recent analyses found resolved excess $^{60}$Ni in one Semarkona chondrule (Tang and Dauphas, 2015). The $(^{60}$Fe/$^{56}$Fe)$_{BS}$ ratios inferred from bulk chondrule analyses are all consistent with <3 x 10$^{-8}$. An initial ratio at this level is more consistent with $^{60}$Fe being inherited from the galactic background (i.e., material from the interstellar medium inherited by the Sun’s molecular cloud; Huss et al., 2009), and would be an insignificant source of heat for planetary differentiation (Moskowitz and Gaidos, 2011).

Initial ratios inferred from in situ Fe-Ni analyses often paint a different picture. Kita et al. (2000) analyzed olivine from one Semarkona chondrule, but did not observe resolved excesses in $^{60}$Ni. However, subsequent in situ analyses of troilite in unequilibrated ordinary chondrites (UOCs) by Tachibana and Huss (2003) found excess $^{60}$Ni that correlated with the Fe/Ni ratios. They inferred $(^{60}$Fe/$^{56}$Fe)$_{BS}$ for sulfides from Bishunpur and Krymka of (1–2) x 10$^{-7}$, an order of magnitude higher than initial ratios inferred from bulk analyses. Mostefauoi et al. (2005) analyzed troilite and magnetite from Semarkona and inferred an even higher initial ratio for sulfides of 1 x 10$^{-6}$. However, because sulfides are easily altered by mild thermal metamorphism (Guan et al., 2004, 2007) researchers later shifted their gaze to Fe-rich silicates, olivine and pyroxene. Tachibana et al. (2006) infer initial ratios of (2–3) x 10$^{-7}$ from in situ analyses of Semarkona and Bishunpur chondrules, while Mishra et al. (2010) inferred higher initial ratios of up to 6 x 10$^{-7}$ from similar analyses. However, Telus et al. (2012) show that the high initial ratios inferred from most of the previous in situ Fe-Ni analyses are artifacts from the way the isotope ratios were calculated. Isotope ratios calculated from counting data have a positive bias, and the bias is inversely proportional to the number of counts in the denominator of the ratio (Ogliore et al., 2011). The low Ni contents of our samples can potentially lead to significant ratio bias. The bias was accentuated in the early work because the final isotope ratios were calculated from the mean of ratios of a large number of measurement cycles. When the isotope ratios from various studies (Tachibana and Huss, 2003; Guan et al. 2007; Tachibana et al., 2006; Tachibana et al., 2007; Tachibana et al., 2009; Telus et al., 2011) were calculated using total counts and bias was suppressed, evidence for $^{60}$Fe disappeared for sulfides and most chondrules (Telus et al., 2012). Nevertheless, evidence for $^{60}$Fe in some chondrules remains, with inferred initial ratios ranging from 2 x 10$^{-7}$ (Telus et al., 2012) to 1 x 10$^{-6}$ (Mishra and Goswami, 2014; Mishra and Chaussonid 2014), though the isochrons are often not well constrained. The presence of $^{60}$Fe at this abundance in the early solar system is consistent with a recent supernova injection of $^{60}$Fe and possibly other short-lived radionuclides in the solar system (Hester and Desch, 2005; Huss et al., 2009; Ouellette et al., 2009; Mishra and Goswami, 2014), although an AGB star of >5 solar masses could also potentially provide sufficient $^{60}$Fe (Wasserburg et al., 2006). Also, an abundance of this magnitude would have important implications for planetary differentiation models (Moskowitz and Gaidos, 2011).

Here, we present $^{60}$Fe-$^{60}$Ni isotopic data for ferromagnesian silicates in chondrules from unequilibrated ordinary chondrites (UOCs) determined in situ using the ion microprobe at the University of Hawai‘i. In interpreting these data, we take into account the clear evidence for late-stage redistribution of Fe and Ni in these chondrules, as demonstrated by synchrotron X-ray fluorescence studies (Telus et al., 2016). We find that most chondrules do not show resolved excesses of $^{60}$Ni. Some chondrules have resolved excesses in $^{60}$Ni, and some measured excesses are large (up to ~70%). Model isochrons constructed for these chondrules typically show a weak correlation between excess $^{60}$Ni and Fe/Ni, indicating that secondary processing disturbed the Fe and Ni isotopic system. Despite this, these chondrules provide useful constraints on the upper and lower limits of the initial $(^{60}$Fe/$^{56}$Fe) of the Solar System.
2. METHODS

2.1. Sample selection

We analyzed olivine and pyroxene from chondrules in the unequilibrated ordinary chondrites Semarkona (LL3.00), QUE97008 (L3.05), EET90161 (L3.05), Bishunpur (LL3.1) and Krymka (LL3.2). We analyzed a wide variety of chondrules (Type I, Type II, cryptocrystalline, barred and porphyritic), but most of the chondrules are Type II porphyritic chondrules. Our primary selection criteria were for chondrules with high enough Fe/Ni to permit us to resolve excess $^{60}\text{Ni}$ and grains large enough to accommodate the ion probe pits. At first, we scanned for suitable chondrules using the electron microprobe (JEOL JXA-8500F) at the University of Hawai‘i (UH). We carried out spot analyses with a 10 μm, 200 nA beam at 20 keV to help constrain Fe/Ni. However, the Fe/Ni ratios were often difficult to constrain because the Ni content in the pyroxene grains are generally below the detection limit of the electron probe. Therefore, we turned to using the ion probe for a second scan of suitable chondrules that passed the electron probe screening. We simply checked the Fe/Ni ratio for a few areas of each chondrule using a 3 nA $^{16}\text{O}$ beam on the Cameca ims 1280 ion microprobe at UH. This method provided more accurate constraints on Fe/Ni.

We focused most of our efforts on chondrule pyroxenes from UOCs because pyroxenes have high $^{56}\text{Fe}/^{54}\text{Ni}$ (e.g., $>2 \times 10^5$) and are less susceptible to thermal metamorphism compared to olivine and sulfides. Also, UOCs of petrologic types 3.00-3.2 have experienced relatively low metamorphic peak temperatures ($<400 ^\circ\text{C}$; Huss and Lewis, 1994). Despite all these benefits, X-ray fluorescence maps in Telus et al. (2016) show that Fe and Ni are mobile in UOCs along chondrule fractures. These fractures are often too fine for us to notice or avoid or they are subsurface features we cannot readily detect with the electron probe or ion probe. Therefore, we also carried out X-ray fluorescence mapping at the Australian Synchrotron and the Advanced Photon Source to scan for suitable chondrules that do not show evidence for Fe or Ni mobilization, along with having large grain sizes and high Fe/Ni. Our best chondrules from this survey are SMK1805 chT and SMK312B chQ from Semarkona, a type 3.00 ordinary chondrite. These chondrules met every criterion mentioned above except that they show evidence for Fe mobilization along chondrule fractures. We did not find chondrules that meet every criterion. Finding suitable chondrules for SIMS Fe-Ni analyses is challenging, which may limit its use for constraining the initial ($^{56}\text{Fe}/^{54}\text{Fe}$)$_{SS}$.

2.2. Secondary ion mass spectrometry

The UOC chondrules were measured using the Cameca ims 1280 ion microprobe at the University of Hawai‘i (UH). Iron and Ni isotopes were measured as positive ions using a 3–10 nA $^{16}\text{O}$ beam, rastered over 15 μm. Spot sizes ranged from 20 to 40 μm and spots were presputtered (180 s) to minimize surface contamination. The secondary-ion beam was automatically centered in the field aperture using the dynamic transfer deflectors at the beginning of each measurement. Terrestrial standards (San Carlos olivine, San Carlos pyroxene, and hypersthene) were generally measured using lower beam currents (1–3 nA) because of their higher Ni contents. We also used synthetic pyroxene standards, JHpx1 and JHpx2 made in the Volcanology and Experimental Petrology lab at UH (see on-line supplementary information). We used two basic SIMS protocols: monocollection and multicollection.

**Monocollection:** Nickel ions ($^{60}\text{Ni}^+$, $^{61}\text{Ni}^+$, and $^{62}\text{Ni}^+$) were counted sequentially on the monocollector electron multiplier, while the Fe ions ($^{56}\text{Fe}^+$ or $^{57}\text{Fe}^+$) were counted on the monocollector Faraday cup (L1) together with $^{60}\text{Ni}$. The main advantage to using monocollection mode is that the monocollector electron multiplier is large and stable, meaning that changes in the gain of the detector over an analytical session are negligible. Also, any changes in the efficiency of the electron multiplier are cancelled out by taking ratios. The electron multiplier can easily handle all Ni count rates that we encountered (up to 5 $\times 10^4$ cps; typical count rates ranging from 100 to 1000 cps). The disadvantage is that measurement times are longer since each isotope is counted separately, and fluctuation of secondary ion beam intensity either due to primary beam instability or heterogeneity of Ni contents introduces additional uncertainties in measured Ni isotope ratios. For our most recent monocollection analyses, $^{60}\text{Ni}^+$, $^{61}\text{Ni}^+$, and $^{62}\text{Ni}^+$ were counted for 2, 50, and 10 s, respectively. Thus, each cycle for monocollection required at least 64 s (not including the time necessary to switch between the different masses and time for mass calibration and energy scans). Mass calibration was done automatically every 25 cycles, and energy scans were done every 50 cycles in order to account for sample charging. A typical measurement of 100 cycles lasted 2 hours.

**Multicollection:** In most cases, Fe and Ni ions were measured simultaneously, with $^{60}\text{Ni}^+$, $^{61}\text{Ni}^+$, and $^{62}\text{Ni}^+$ counted on electron multipliers and $^{56}\text{Fe}^+$ measured on a Faraday cup. Sometimes, we set Ni and Fe on separate B-fields and jumped from one to the other. This minimizes the effects of off-axis aberrations and gives the multicollector electron multipliers a rest every cycle. Mass calibration and energy scans were done automatically every 50 cycles. Each measurement cycle lasted 30 seconds and a measurement consisted of 200 cycles; a typical measurement lasted 2 hours. The multicollector electron multipliers are less stable with the gains changing throughout the analytical session (average $^{60}\text{Ni}/^{62}\text{Ni}$ ratio change of $\sim$10%), especially if they have been bombarded with high counts from Ni-rich phases. Unlike monocollection measurements, the gain changes among multicollection electron multipliers introduce inaccuracy in Ni isotope ratios; thus, a correction for drift in the gain of the detectors must be made using standard-sample bracketing. Chondrules BM80 ch37 and QUE ch3 were measured in both monocollection and multicollection mode (Table 1).

The gain of the multicollection electron multipliers degrades quickly during a series of measurements. For this study, we checked the pulse height distribution and adjusted the voltage on the electron multipliers in order
to optimize the gain of the detectors at the beginning of each SIMS session. We made no further adjustments during the day. We analyzed standards several times to characterize the gains at the beginning of the measurement session. Then we measure the standards throughout each day and use sample-standard bracketing to monitor and correct for drift in the gains of the detectors.

**Molecular interferences:** To resolve major molecular interferences on the Ni isotopes (e.g., $^{44}\text{Ca}^{16}\text{O}o \text{n}^{60}\text{Ni}$, $^{45}\text{Sc}^{16}\text{O}o \text{n}^{61}\text{Ni}$, and $^{46}\text{Ca}^{16}\text{O}o \text{n}^{62}\text{Ni}$), a mass resolving...
power (MRP) of ~4500 was used during multicollection analyses and a MRP of 6000–7000 was used during monocollection analyses. However, this does not resolve the $^{60}\text{Ni}$ hydride on $^{61}\text{Ni}$ (requires MRP = 8124). To evaluate the influence of $^{60}\text{NiH}$ on $^{61}\text{Ni}$, we carried out high-resolution scans with MRPs >8000 during each SIMS session. We consistently found the $^{60}\text{NiH}$ peak and other hydrides (e.g., $^{59}\text{CoH}$ on $^{60}\text{Ni}$ and $^{60}\text{NiH}$ on $^{62}\text{Ni}$) to contribute less than 1‰ to the Ni isotopes for both standards and samples (e.g., Fig. 1 and on-line supplementary files). Interferences were often measured during each measurement (via peak jumping) or after each measurement (by deflecting the secondary beam). We also tried to address the possible influence of unresolved complex molecular interferences on our analyses, such as the $[^{56}\text{Fe}^{64}\text{Zn}]^{2+}$ interference on $^{60}\text{Ni}$ (resolved with MRP = 47,190). Similar to Mishra and Goswami (2014), we did not find any significant counts associated with complex molecular interferences. The contribution of tails of the interferences on the Ni peaks is discussed in Section 2.3.

Uncertainties in the relative sensitivity factor ($^{56}\text{Fe}^{60}\text{Ni}_{\text{true}}$/$^{56}\text{Fe}^{61}\text{Ni}_{\text{measured}}$) can stem from using different beam currents for the standards and samples or using non-matrix-matched standards. The Fe and Ni content of chondrule pyroxene compositions range from 4 to 7 at.% and <0.01 at.% respectively. The Fe and Ni content for our synthetic standard and hypersthene standard are very similar to those of our chondrules, but we often use San Carlos pyroxene, which has an Fe content of 1.7 at.% and Ni of 0.03 at.%, quite different from our samples. To deal with the different sensitivity factors, we apply a relative sensitivity factor correction to the Fe/Ni ratios. The Fe/Ni ratio varies with time during a SIMS measurement. This can result in variations in the relative sensitivity factor depending on the length of the measurements. To account for this, we measure standards and samples for the same amount of time, even though we do not require all the cycles to get the precision we need on the standards.

### 2.3. Data analysis

Calculating isotope ratios from counting data results in a positive bias that correlates inversely with the number of counts of the normalizing isotope (Ogliore et al., 2011). Calculating ratios by averaging the ratios from the measurement cycles makes this problem worse because a cycle has fewer counts than the total measurement. The measured Fe/Ni ratios vary by up to one order of magnitude. Because the Fe concentration varies by only a few percent, the variation in Fe/Ni ratio is almost entirely due to the Ni concentration. Thus, the higher the Fe/Ni ratio, the lower the Ni counts and the greater the bias in the Ni-isotope ratio. This produces a correlation on an isotope plot that resembles an isochron. Ratio bias propagates into the slope of the isochron in different ways depending on how the data are reduced. For the $^{60}\text{Fe}$-$^{60}\text{Ni}$ system, an internal mass-fractionation correction using biased ratios produces a positive bias in the slope of the isochron when normalizing with $^{61}\text{Ni}$, or a small negative bias in the slope when normalizing with $^{62}\text{Ni}$ (Telus et al., 2012). In order to significantly reduce the effect of ratio bias, isotope ratios reported here were calculated from total counts, a less-biased method of calculating ratios (Ogliore et al., 2011). This method involves summing the counts of the numerator isotope over all cycles and dividing by the summed counts of the denominator isotope over all cycles (time interpolation is done for monocollection to account for the differences in count times of the different isotopes). To further ensure that ratio bias is not an issue, we check that the data normalized to $^{61}\text{Ni}$ and $^{62}\text{Ni}$, which differ in abundance by a factor of ~3, are consistent.

Since we collected the data in cycles, we were able to include time interpolation and remove anomalous cycles due to spikes in the detector signal from Ni-rich phases, electronic noise, or primary beam dropout. The data were corrected for electron multiplier background (typically measured overnight at the end of the session for 5–10 h.
without the primary beam) and electron multiplier deadtime. Drift in the electron multiplier gain was corrected using sample-standard bracketing. Extraneous counts on the Ni peaks from the tails of interferences were determined using the tail-to-peak ratio (~1 × 10⁻³), which was determined from measuring counts at the Ni peaks and counts at a few points along the tails, to the low-mass side of each peak (see on-line supplementary files). Contributions of tails of interferences onto Ni isotope counts are typically less than 1‰. However, chondrules QUE chC, SMK312B chE, BM23 ch13, BM23 ch37 (multicollection), and QUE ch3 (July 2013) show evidence for interference contributions that are higher than typical values (up to 5‰). Interference corrections were applied for these chondrules (except for SMK312B chE) and are provided in the supplementary files. The interference correction did not make a significant difference in the inferred initial ratio for these chondrules and are not used for the initial ratios reported in Table 1.

Uncertainties on the measured ratios include the standard error of the ratios calculated from individual cycles and uncertainties propagated from standard-sample bracketing. This allows us to account for non-statistical cycle-to-cycle uncertainties propagated from standard-sample bracketing. Drift in the electron multiplier gain was corrected using sample-standard bracketing. Extraneous counts on the Ni peaks from the tails of interferences were determined using the tail-to-peak ratio (~1 × 10⁻³), which was determined from measuring counts at the Ni peaks and counts at a few points along the tails, to the low-mass side of each peak (see on-line supplementary files). Contributions of tails of interferences onto Ni isotope counts are typically less than 1‰. However, chondrules QUE chC, SMK312B chE, BM23 ch13, BM23 ch37 (multicollection), and QUE ch3 (July 2013) show evidence for interference contributions that are higher than typical values (up to 5‰). Interference corrections were applied for these chondrules (except for SMK312B chE) and are provided in the supplementary files. The interference correction did not make a significant difference in the inferred initial ratio for these chondrules and are not used for the initial ratios reported in Table 1.

Uncertainties on the measured ratios include the standard error of the ratios calculated from individual cycles and uncertainties propagated from standard-sample bracketing. This allows us to account for non-statistical cycle-to-cycle variations during each measurement. To calculate excess in ⁶⁰Ni for each spot analysis from each chondrite analyzed in this study, the superimposed crosses indicate analyses done in monocollection mode, all others were measured in multicollection mode. Errors are 2σ.

Using Isoplot Model 1 fit, the initial ⁵⁶Fe/⁶⁰Fe ratio for each chondrule is inferred from the error-weighted regression of ⁶⁰Ni/⁶²Ni (or ⁶⁰Ni/⁶¹Ni) vs. ⁵⁶Fe/⁶²Ni (or ⁵⁶Fe/⁶¹Ni). Uncertainties on the isochron slopes are reported as 2σ, or as 95% confidence errors when the probability of fit is less than 15% (or MSWD is very large). For each isochron, we report the mean square weighted deviation (MSWD), which characterizes how well the data fit the regression. The MSWD is the same as the reduced Chi squared; the term historically used for this parameter in statistics. Well-correlated regressions will have MSWDs close to 1. Detailed calculations for the data analyses are provided in the supplementary file for each chondrule.

3. RESULTS

3.1. Δ⁶⁰Ni values

The ⁶¹Ni- and ⁶²Ni-normalized Ni isotope ratios and the Fe/Ni ratios for each chondrule analyzed in this study are provided in the on-line supplementary material. Fig. 2 shows the Δ⁶⁰Ni values for each spot analysis from each chondrule reported here. There is considerable scatter in the data, but most are indistinguishable from zero. Of the 24 chondrules analyzed for this study, a few chondrules have resolved excesses in ⁶⁰Ni of up to ~70‰. Negative values were determined for some spot analyses. Many of the highly negative values were obtained by monocollection. In the following section, we determine which chondrules provide the best constraints on the initial ⁵⁶Fe/⁶⁰Fe ratio of UOCs.

3.2. Initial ⁵⁶Fe/⁶⁰Fe ratio of UOC chondrules

It is important to calculate the initial ratios using both the ⁶¹Ni and ⁶²Ni normalization to monitor the extent of ratio bias, which propagates into the isochron differently depending on how the mass-fractionation correction is made and depending on which normalizing isotope is used (Telus et al., 2012). An internal mass-fractionation of biased ratios using ⁶²Ni/⁶⁰Ni results in under-correcting the ⁶⁰Ni/⁶¹Ni ratios and introducing a positive bias in the inferred initial ratio. When the ⁶²Ni normalization is used instead, an internal mass-fractionation correction results in over-correcting the ⁶⁰Ni/⁶²Ni ratios, producing a negative bias in the initial ratio. Also, since ⁶²Ni has more counts, using it as the normalizing isotope generally gives results that are less biased. When the ratios are calculated by summing the counts from all cycles of a measurement instead of averaging the ratios from each cycle (Ogliore et al., 2011), the choice of normalizing isotope for the nickel isotope ratios (⁶¹Ni or ⁶²Ni) does not change the result. However, the uncertainty for ratios normalized to ⁶²Ni is systematically larger than for ratios normalized to ⁶¹Ni due to the internal mass-fractionation correction (the uncertainty on the ⁶¹Ni/⁶²Ni ratio is multiplied by 2). Initial ratios determined from ratios normalized to ⁶¹Ni and ⁶²Ni are consistent (see supplementary files). For the rest of this paper, we refer only to ⁶²Ni-normalized ratios.
Fig. 3. Initial $^{60}\text{Fe}/^{56}\text{Fe}$ ratios of UOC chondrules determined without forcing the intercept (solid symbols) and with forcing the intercept (light grey symbols). Points with crosses were measured in monocollection mode, while all others were analyzed in multicollection mode (see Section 2 for details). Tie lines indicate analyses for the same chondrule but different analytical sessions.

Fig. 4. Backscattered electron image and model isochrons for QUE 97008 chondrule chC (top) and Krymka chondrule KRM94 ch1 (bottom). The Y-axis is the fractionation-corrected $^{60}\text{Ni}/^{62}\text{Ni}$ ratios (left) and the excess in $^{60}\text{Ni}$ in permil (right). Despite the high Fe/Ni, the inferred initial ratios are unresolved from zero. The fine lines mark the error envelope and the grey horizontal line marks the terrestrial $^{60}\text{Ni}/^{62}\text{Ni}$ composition.
To determine which chondrules provide the best constraints, we determined the initial ratio in two ways: with and without forcing the regression through the terrestrial composition (e.g., \( \frac{^{56}\text{Fe}}{^{62}\text{Ni}} = 0.001 \pm 0.001 \) and \( \frac{^{60}\text{Ni}}{^{62}\text{Ni}} = 7.215 \pm 0.005 \)). The initial ratios are summarized in Table 1 and Fig. 3. Several chondrules have results that differ significantly when the intercept is forced through the terrestrial composition. This includes SMK DAP1 (Sept. 2011), SMK 1805-5 (July 2010), SMK312B chE, SMK312B chT, QUE chI, BM80 ch37 multi, BM80 r40, and BVG ch1. In some cases, the large difference between the inferred initial ratios is due to a limited range in the Fe/Ni and/or the Ni-isotope ratios (e.g., SMK 1805-5 (July 2010), SMK312B chE, SMK312B chT, BM80 r40, and BM80 ch37 multi). For these datasets, the slope is better constrained when the intercept is forced through terrestrial. However, the inconsistencies in the inferred initial ratio for SMK DAP1 (Sept. 2011), QUE chI, and BVG ch1 are due to large positive or negative offsets in the Ni-isotopic composition of the chondrules from terrestrial. For instance, spot analyses for SMK DAP1 (Sept. 2011) have Ni-isotopic compositions that are significantly higher than the terrestrial composition that was not observed for previous sessions (e.g., SMK DAP-1 (July 2010)). The difference between sessions may be due to differences in the analytical methods (e.g., smaller spot size), but we cannot say for certain why there is this difference. Spot analyses for chondrules QUE chI and BVG ch1 have Ni-isotopic compositions that are much lower than the terrestrial standards.

Many chondrules have essentially the same initial ratio regardless of how the isochron is determined. Most of these are indistinguishable from zero, including SMK DAP1 (July 2010), SMK DAP2, SMKMT r1, SMK312 chQ, QUE ch3, QUE chK, QUE chC, QUE chF, QUE ch6, EET r1, BM23 ch13, BM23 ch9, BM23 ch12, and KRM94 ch1. A few of these chondrules have resolved initial ratios. Bishunpur chondrules, BM80 ch13 and BM80 ch37, have a resolved initial ratio of \((4.9 \pm 4.4) \times 10^{-7}\) and \((3.1 \pm 3.0) \times 10^{-7}\), respectively when the intercepts are forced through terrestrial. With the large scatter in the \( \frac{^{60}\text{Ni}}{^{62}\text{Ni}} \) ratios and the very large MSWD of 20 and...
24, it is clear the Fe-Ni systematics of these chondrules have been disturbed. Krymka radial pyroxene chondrule, KRM93 ch11, consistently gives a resolved initial ratio of \( \frac{2.0}{10^7} \) from two different datasets, regardless of whether the intercept is forced through terrestrial. Details for each dataset are available in the supplementary information.

3.3. Chondrules with unresolved initial ratios, despite high Fe/Ni ratios

Some of our chondrules have very high Fe/Ni, but do not show evidence for excess \(^{60}\)Ni. For example, QUE97008 chC and Krymka chondrule KRM94 ch1 are large cryptocrystalline chondrules with high Fe/Ni (>1 \( \times 10^6 \)), but the inferred initial ratios are unresolved from zero (Fig. 4). With such high Fe/Ni and uncertainties of \( \sim 5\% \) on \(^{60}\)Ni, an initial ratio >1 \( \times 10^7 \) should be easily resolved.

3.4. Chondrules with resolved initial \(^{60}\)Fe/\(^{56}\)Fe ratios

The data for Bishunpur chondrule BM80 ch13, a porphyritic olivine-pyroxene chondrule, gives an initial ratio of \((4.9 \pm 4.4) \times 10^{-7}\) with an MSWD of 20 when the intercept is forced through the terrestrial composition (Fig. 5). The initial ratio is similar without the forced intercept, except the uncertainty is much larger. Bishunpur BM80 ch37 is a large (>1 mm) cryptocrystalline pyroxene chondrule. The initial ratio inferred from the monocollection data set is \((3.0 \pm 3.1) \times 10^{-7}\) with an MSWD of 24 when the intercept is forced through the terrestrial composition (Fig. 5). It is heavily bleached, but we avoided the obviously bleached zones. This chondrule was analyzed in two different modes, monocollection mode (black circles) and multicollection mode (grey circles). The monocollection data are more scattered than the multicollection analyses. Many monocollection spot analyses exhibit large positive values for \(^{60}\)Ni (up to 70\%), but also large negative values (up to -40\%). The \(^{56}\)Fe/\(^{52}\)Ni span a wide range for the monocollection data, while those for multicollection form a relatively tight cluster around 2.5 \( \times 10^5\). The scatter in the data for both of these chondrules is likely from Fe-Ni mobilization (see supplementary material in Telus et al., 2016).

Krymka chondrule KRM93 ch11 is a large (>1 mm) heavily fractured cryptocrystalline pyroxene chondrule (Fig. 6). Submicron sulfide blebs are also pervasive in this chondrule and were impossible to avoid for our spot analyses. We aimed to avoid large fractures but many of the fine fractures could not be avoided. This chondrule was analyzed on two separate occasions and the results are consistent (Table 1). When the intercept is forced through terrestrial, the inferred initial ratio from the July 2011 measurements is \((1.7 \pm 0.6) \times 10^{-7}\) and that for the December 2008 measurements is \((2.3 \pm 0.9) \times 10^{-7}\); combined, the initial ratio is \((2.2 \pm 0.7) \times 10^{-7}\) with an MSWD of 10.1 (Fig. 6). This chondrule appears to provide our strongest constraints on the initial \(^{60}\)Fe/\(^{56}\)Fe ratio of UOC chondrules.

4. DISCUSSION

We have presented Fe-Ni SIMS data of UOC chondrules that were collected over the past several years. Most of the chondrules do not show resolved excesses in \(^{60}\)Ni (Fig. 2). The initial \(^{60}\)Fe/\(^{56}\)Fe for UOC chondrules inferred from our analyses are mostly unresolved (Table 1, Fig. 3), but a few show large excesses in \(^{60}\)Ni and resolved initial ratios (Figs. 5 and 6). Here, we discuss complications from Fe-Ni redistribution on placing constraints on the initial \(^{60}\)Fe/\(^{56}\)Fe ratio of UOC chondrules (Telus et al., 2016) and we place some constraints on the upper and lower limits of the initial \(^{60}\)Fe/\(^{56}\)Fe ratio of UOC chondrules.

4.1. Complications from Fe-Ni mobilization in UOC chondrules

It is often assumed that olivine and especially pyroxene remained closed for Fe and Ni in chondrules from UOCs because volume diffusion of Ni in these phases should be
in situ analyses that incorporate extraneous Fe will have higher Fe/Ni ratios, moving points to the right on the isochron diagram and resulting in lower inferred initial ratios. Inclusion of extraneous Fe and Ni in chondrule fractures may not affect all spot analyses. If one could isolate only those measurements that did not incorporate extraneous Fe and Ni, reliable results could be obtained. A mixture of "good" and "bad" points will give poorly correlated isochrons (Telus et al., 2016). Also, lattice diffusion of Ni from olivine or pyroxene into sulfide or metal blebs can result in poorly correlated isochrons if some SIMS spots incorporate metal/sulfide blebs located within pyroxene grains, while others do not.

4.2. Interpretation of unresolved initial ratios

Our ability to resolve initial ratios using our in situ analyses is limited by the uncertainties on the Ni isotope ratios. Initial ratios >2×10^{-7} should be resolved with in situ analyses if Fe/Ni are sufficiently high. However, chondrules may not show resolved excesses in 60Ni if they formed after a significant amount of 60Fe had already decayed. For instance, if the initial solar system 60Fe/56Fe ratio was 2×10^{-7}, then chondrules that formed >2.6 Ma after solar system formation (i.e., after 1 half-life of 60Fe) would have an initial ratio of <1×10^{-7}, which we cannot always resolve with the current in situ techniques.

On the other hand, synchrotron maps from Telus et al. (2016) indicate that redistribution of Fe and Ni can result in lower inferred initial ratios. For example, Krymka chondrule KRM94 ch1 and QUE97008 chC have high 56Fe/60Ni ratios (>1×10^6), but the inferred initial 60Fe/56Fe ratios are unresolved (Table 1, Fig. 4). Synchrotron XRF maps of KRM94 ch1 show extensive Fe-Ni mobilization along the chondrule fractures, with many of our spot analyses overlapping these fine fractures (see Fig. 11 in Telus et al., 2016). This indicates that the low initial ratio for this chondrule likely does not reflect its true initial ratio. Telus et al. (2016) also found that almost all chondrules from UOC finds show extensive Fe-Ni redistribution; thus, in situ analyses of chondrules from QUE 97008 and EET 90161 may also be compromised in this way. Bulk analyses of chondrules from finds (Tang and Dauphas, 2012a; Spivak-Birndorf et al., 2012a, 2012b) are also likely affected by extraneous Fe and Ni.

4.3. Estimating the lower limit on 60Fe/56Fe of the UOC chondrule-forming region

The observed excesses in 60Ni and Fe/Ni can be used to place constraints on the initial 60Fe/56Fe. We find 60Ni excesses up to ~70‰ (Fig. 5 and 6). The presence of excess 60Ni of this magnitude in Fe-rich igneous objects indicates that the excesses come from the decay of 60Fe. Nonradiogenic Ni isotope anomalies are not this large (e.g., Birck and Lugmair, 1988; Chen et al., 2009) and would have likely been reduced by mixing with normal Ni during the melting and crystallization that produced chondrules.

Redistribution of Fe and Ni can decrease Δ60Ni, but it cannot increase them. Decreases in Δ60Ni can be achieved by adding terrestrial Ni, while increasing Δ60Ni would require additional input of only 60Ni and not the other Ni isotopes, which is highly unlikely. Therefore, we can use the highest Δ60Ni values of ~70‰ to help constrain the true initial 60Fe/56Fe ratios prior to Fe-Ni redistribution. Below, we discuss constraining the lower limit of the initial 60Fe/56Fe for UOC chondrules by determining the initial ratio consistent with the largest possible Fe/Ni and the largest Δ60Ni values for UOC chondrules.

It is possible that the high initial ratios inferred from in situ analyses are a result of redistribution of Fe and Ni.
This could occur by decreasing Fe/Ni via preferential loss of Fe or by concentrating the radiogenic nickel in specific phases. This would mean that the Fe/Ni ratios during the decay of $^{60}$Fe were higher than what we now observe. The maximum $^{56}$Fe/$^{62}$Ni we have measured in our chondrules is $3 \times 10^6$ (e.g., EET r1). Constraining the highest possible Fe/Ni prior to Fe-Ni redistribution is not straightforward, but we know that the initial Fe/Ni ratios of chondrule Fe-silicates cannot be infinitely large, since their values are limited by partitioning among phases. We have taken a $^{56}$Fe/$^{62}$Ni ratio of $3 \times 10^6$ as an upper limit for the highest possible Fe/Ni ratio. This is significantly higher than what we have observed for any of our analyses.

To constrain the lowest initial $^{60}$Fe/$^{56}$Fe that could have produced the observed excesses in $^{60}$Ni after Fe-Ni redistribution, we use our estimate of the largest possible Fe/Ni together with the observed excesses in $^{60}$Ni from chondrules with resolved initial ratios to place constraints on the initial $^{60}$Fe/$^{56}$Fe of UOCs. Fig. 7 compares initial ratios from $1 \times 10^7$ to $3 \times 10^6$ with the data for chondrules with resolved initial ratios. In order to produce excesses in $^{60}$Ni of $70^{\circ}\text{e}$, a lower limit on the initial ratio of $2 \times 10^7$ is required based on a maximum $^{56}$Fe/$^{62}$Ni ratio of $3 \times 10^6$. However, only one chondrule (BM80 ch37 monocollection) has such large excesses in $^{60}$Ni. Excesses of $20^{\circ}\text{e}$, observed for other chondrules, require a lower limit of $5 \times 10^6$. The limitation of this exercise is that the value chosen for the Fe/Ni ratio prior to the assumed disturbance of the Fe-Ni system in the chondrule is unknown. If the Fe/Ni prior to the disturbance were significantly larger than our estimate of $3 \times 10^6$ for $^{56}$Fe/$^{62}$Ni, this would result in an initial $^{60}$Fe/$^{56}$Fe that is lower than our estimate. We do not have evidence for Fe/Ni in chondrules that are higher than our estimate.

Our estimate of $5 \times 10^{-8}$ as the lower limit on the initial $^{60}$Fe/$^{56}$Fe of UOC chondrules means that decreasing Fe/Ni by losing Fe or concentrating anomalous Ni can potentially produce excesses in $^{60}$Ni of $20^{\circ}\text{e}$ provided that the true initial ratio was at least $5 \times 10^{-8}$. The mechanism for decreasing Fe/Ni is not clear, but may involve redistribution of Ni from pyroxenes into secondary metal/sulfide blebs during thermal metamorphism. In situ analyses of pyroxenes that include these secondary phases will have apparently low Fe/Ni, but relatively high $\Delta^{60}$Ni values, moving points to the left on the isochron plot (see Fig. 13).
than 20 sured excess in 60Ni cannot be explained if the initial ratio (Fig. 7). This is a stronger constraint because the mea-
mated based on summing the Gaussian distributions of
artificially high Fe/Ni and low D can increase the Fe/Ni ratio (by adding Fe) and move points toward the intercept (by adding Ni), resulting in artificially high Fe/Ni and low Δ60Ni values and resulting in lower inferred initial 60Fe/56Fe. Interestingly, chondrules with resolved initial ratios have 56Fe/62Ni of up to 5 × 10^5 (e.g., Figs. 5–7), while those with very high 56Fe/62Ni (up to 1 × 10^6) do not show evidence for excess 60Ni (e.g., Fig. 4).

4.5. Our best estimate of 60Fe/56Fe in the region where UOC chondrules formed

Due to complications from Fe-Ni mobilization, it is difficult to constrain the initial 60Fe/56Fe ratio of UOCs. An upper limit of 3.0 × 10^{-7} for UOC chondrules is estimated based on summing the Gaussian distributions of the inferred initial ratios (Figs. 8). We constrain the lower limit to be 5 × 10^{-8} based on excesses in 60Ni of more than 20% from chondrules with resolved initial ratios (Fig. 7). This is a stronger constraint because the measured excess in 60Ni cannot be explained if the initial ratio was significantly lower than this value. Previously reported in situ Fe-Ni systematics of UOC chondrules by Mishra and Goswami (2014) and Mishra and Chausiod (2014) give higher initial ratios than the chondrules with resolved initial ratios reported in this study. Since these studies use similar analytical techniques, data analyses and samples, the apparent discrepancy between in situ analyses from this study and previous SIMS studies from Mishra remains unresolved.

4.6. Comparison with ICPMS and TIMS UOC chondrule data

Bulk analyses of chondrules from NWA5717 (UG3.05) and QUE97008 (L3.05) do not give resolved excess 60Ni and do not show any correlation between excess 60Ni and Fe/Ni (Tang and Dauphas, 2012a; Spivak-Birndorf et al., 2012a; Chen et al., 2013). Chondrules from Chaipur (L3.4) also do not show resolved excess 60Ni (Spivak-Birndorf et al., 2012b; Tang and Dauphas, 2012a); however, this is likely because this chondrite experienced significant thermal metamorphism with a peak temperature >400 °C (Huss and Lewis, 1994). The initial 60Fe/56Fe for UOCs inferred from these studies are all consistent with <3 × 10^{-8}, inconsistent with initial ratios between 5 × 10^{-8} and 3.0 × 10^{-7} inferred from this study.

Tang and Dauphas (2015) focused their most recent bulk chondrule analyses on those from Semarkona because they show the least evidence for Fe-Ni mobilization. They analyzed 6 chondrules and found evidence for excess 60Ni (0.051 ± 0.043‰) in one, a Type II (Fe-rich) Semarkona chondrule. From their data, they infer an initial 60Fe/56Fe for UOCs of (5.4 ± 3.3) × 10^{-9}, consistent with the upper limit of <3 × 10^{-8} inferred from previous bulk chondrule studies. Based on preliminary results from synchrotron X-ray fluorescence mapping of UOC chondrules that found that 5 out of 16 (or 31%) of Semarkona chondrules were affected by Fe-Ni mobilization (abstract by Telus et al., 2013), Tang and Dauphas (2015) assume that most bulk analyses of Semarkona chondrules should be unaffected by Fe-Ni redistribution. However, additional synchrotron X-ray maps of Semarkona chondrules reported by Telus et al. (2016) show that 17 of 27 (or 63%) of chondrules from Semarkona exhibit clear evidence for Fe and/or Ni mobilization. Tang and Dauphas (2015) argue that parent-body disturbance will produce low Fe/Ni and that chondrules with high Fe/Ni should give reliable results. However, Telus et al. (2016) show that Fe-Ni mobilization introduces extraneous Fe and Ni into the chondrule which can increase the Fe/Ni ratio (by adding Fe) and move towards the intercept (by adding Ni), resulting in artificially high Fe/Ni and low Δ60Ni values and resulting in lower inferred initial 60Fe/56Fe. Interestingly, chondrules with resolved initial ratios have 56Fe/62Ni of up to 5 × 10^5 (e.g., Figs. 5–7), while those with very high 56Fe/62Ni (up to 1 × 10^6) do not show evidence for excess 60Ni (e.g., Fig. 4).

4.7. Coordinated bulk & in situ analyses of UOC chondrules

In collaboration with researchers at CalTech, we carried out coordinated bulk and in situ Fe-Ni analyses of chondrules from QUE97008 and Semarkona (QUE ch3 and SMKDAP-1). The bulk analyses were done using thermal ionization mass spectrometry and the results were reported by Chen et al. (2013). The chondrules were broken and fragments were reserved for in situ analysis. The chondrules were first washed in ethanol and HCl to remove metal or sulfide from the surface and in cracks. Then the chondrules were dissolved in strong acids. The Ni extraction techniques are described in Chen et al. (2009). Initial 60Fe/56Fe inferred from their bulk analyses are unresolved from zero, although a relatively high initial ratio of ~1 × 10^{-7} for QUE ch3 is permitted by the data (Chen et al., 2013). The in situ data for these chondrules are unresolved from terrestrial (Table 1). Additional studies involving coordinated bulk and in situ analyses are necessary to better understand the differences inferred from these two techniques.
4.8. Constraining the source of $^{60}$Fe in the early solar system

4.8.1. Galactic background

An initial $^{60}$Fe/$^{56}$Fe between $5 \times 10^{-8}$ and $3.0 \times 10^{-7}$ for UOCs corresponds to $8.5 \times 10^{-8}$ and $5.1 \times 10^{-7}$ for the initial Solar System $^{60}$Fe/$^{56}$Fe ratio, $(^{60}$Fe/$^{56}$Fe)$_{SS}$, assuming all UOC chondrules formed 2 Ma after CAIs. Iron-60 in the early solar system could have been inherited from the galactic background, defined here (as in Huss et al., 2009) as the average composition of interstellar material from which molecular clouds form. Since S/LRs have rapid decay rates, their abundance in the interstellar medium is generally low. The abundance of $^{60}$Fe in the galactic background is constrained by comparing abundances determined from Galactic chemical evolution models with the present day $^{60}$Fe abundance in the galaxy determined from gamma-ray spectroscopic observations. With a Galactic chemical evolution model to track the buildup of metals from when the galaxy formed (at 12 Ga) to when the solar system formed (at 4.6 Ga) and the present-day gamma-ray emission fluxes of $^{60}$Fe reported by Wang et al. (2007), the background $^{60}$Fe/$^{56}$Fe ratio of $3 \times 10^{-8}$ is determined (see Eq. (14) in Huss et al., 2009). The lower limit of $0.8 \times 10^{-7}$ inferred from out data is marginally above this estimate for galactic background, while our upper limit is well above this estimate. However, this comparison assumes that there is no additional delay time associated with isolating solar system material from the average galactic background (Clayton, 1983; Huss et al., 2009). The initial $^{60}$Fe/$^{56}$Fe of the solar system inherited from the galactic background would be $10^{-9}$ when we consider that newly synthesized material requires 10–100 Ma to mix with the cold interstellar medium (McKee and Ostriker, 1977).

4.8.2. Single stellar sources

Injection of $^{60}$Fe into the budding solar system from a single stellar source has been modeled for asymptotic giant branch (AGB) stars and type II supernovae (SNII). A single stellar source is defined here as a nearby (within a few parsecs) dying star that ejected material immediately prior to the solar system’s formation. This mechanism has been considered a possible trigger for the collapse of the molecular cloud that formed the Solar System (Cameron and Truran, 1977; Boss and Keiser, 2010). During stellar nucleosynthesis, $^{60}$Fe is produced via slow-neutron capture (s-process) on $^{59}$Fe, which has a very short half-life of 44 days. For efficient production of $^{60}$Fe, the neutron density must exceed $10^{30}$ billion in order to get significant neutron capture on $^{59}$Fe through s-process nucleosynthesis (Limongi and Chieffi, 2006). This requires temperatures between $4 \times 10^{5}$ and $2 \times 10^{9}$ degrees.

High temperatures necessary for production of $^{60}$Fe are achieved in the He shell of a 5 $M_\odot$ AGB star, where the $^{60}$Fe/$^{56}$Fe is estimated to be $\sim 1 \times 10^{-6}$ (Wasserburg et al., 2006). Some $^{60}$Fe production can occur through Cool Bottom Processing, which involves mixing material between the cool envelope and hotter and denser layers. Wasserburg et al. (2006) calculate initial $^{60}$Fe/$^{56}$Fe of $4 \times 10^{-8}$ to $2 \times 10^{-7}$ for the envelopes of low mass AGB stars. The major drawback for an AGB source of $^{60}$Fe is that these stars are old objects (relative to the lifetime of molecular clouds) and not associated with star formation regions (e.g., Kastner and Myers, 1994).

Massive stars between 11 $M_\odot$ and 33 $M_\odot$ die as type II supernovae. Nucleosynthesis models indicate that $^{60}$Fe is produced copiously by massive stars (e.g., Limongi and Chieffi, 2006). Ejecta from a supernovae explosion could have potentially been incorporated during solar system formation. Presupernova, conditions for $^{60}$Fe production are achieved during hydrostatic burning in the C and He burning shells (Limongi and Chieffi, 2006). Explosive nucleosynthesis of $^{60}$Fe is most efficient when shock waves generated from the supernova pass through the C burning shell. The drawback for a supernova source of $^{60}$Fe is that it produces excessive amounts of $^{51}$Mn (e.g., Meyer, 2005). In order to better match the yields of supernova models and the initial $^{60}$Fe/$^{56}$Fe, $^{53}$Mn/$^{55}$Mn and $^{26}$Al/$^{27}$Al determined from isotope analyses, mixing at the C/O burning shell and fall back of a significant fraction of ejecta back onto the supernova remnant are required (Takigawa et al., 2008). A supernova source for $^{60}$Fe is more likely than an AGB source because young stellar objects form in clusters where such massive stars are common (Williams and Gaidos, 2007). Wasserburg et al. (2006) calculate an initial $^{60}$Fe/$^{56}$Fe of $2 \times 10^{-5}$ for the ejected stellar envelope of a 15 $M_\odot$ supernova source. The initial solar system $^{60}$Fe/$^{56}$Fe inferred from our chondrule data is consistent with a single supernova as the source for $^{60}$Fe. Nevertheless, some argue that a single supernova source is also unlikely because it is inconsistent with astronomical observations of star formation (e.g., Gounelle and Meynet, 2012; Young, 2014).

4.8.3. Self-enrichment of the molecular cloud

The solar system could have incorporated a $(^{60}$Fe/$^{56}$Fe)$_{SS}$ ratio higher than galactic background if it formed in a molecular cloud complex (i.e., a large molecular cloud that consists of multiple star clusters of different ages) that was enriched in $^{60}$Fe. Here, we define this process as self-enrichment (as in Huss et al., 2009); however, Gounelle and Meynet (2012) use “background” to refer to the same concept. Self-enrichment of the molecular cloud might occur if there was an enhanced abundance of $^{60}$Fe from supernovae of massive stars prior to the solar system’s formation. Self-enrichment is preferred by Gounelle and Meynet (2012) because it provides a realistic mechanism for explaining the relative abundance of $^{26}$Al and $^{60}$Fe, which cannot be readily explained with a simple SN ejection. Gounelle and Meynet explain that $(^{60}$Fe/$^{56}$Fe)$_{SS}$ of $3 \times 10^{-7}$ and the $^{60}$Fe/$^{26}$Al ratio can be explained if $^{60}$Fe came from an older generation of massive stars within a giant molecular cloud (~15 Ma older), instead of one that died immediately before solar system formation. With our estimates of $(0.8–5) \times 10^{-7}$ for the initial Solar System ratio, $(^{60}$Fe/$^{56}$Fe)$_{SS}$, self-enrichment of the molecular cloud described here is possible and perhaps more likely than a single stellar source (Gounelle and Meynet, 2012).

In order to account for higher-than-background initial ratios of S/LRs, Young (2014) incorporates the material ejected by winds from Wolf-Rayet stars, excluding the subsequent supernova explosion, into their GCE model since...
these two ejections are separated in time. Winds from Wolf-Rayet stars have little effect on the $^{60}$Fe abundance (Arnould et al., 2006). Young (2014) try to match the low initial $^{60}$Fe/$^{56}$Fe inferred from bulk measurements, not those inferred from in situ analyses. Estimates of the initial ratio inferred from in situ analyses are not consistent with this model.

4.9. Developing the $^{60}$Fe-$^{60}$Ni system for early solar system chronology

Constraining the initial $^{60}$Fe/$^{56}$Fe of the Solar System is necessary for using the $^{60}$Fe-$^{60}$Ni system for chronology. Although analytical issues from ratio bias have been addressed (Telus et al., 2012), discrepancies between in situ and bulk analyses of UOC chondrules remain. Late-stage open-system redistribution of Fe and Ni was prevalent and provides some explanation for these discrepancies (Telus et al., 2016). This alteration can easily compromise both the bulk and in situ analyses, resulting in either low inferred initial ratios or poorly correlated isochrons. Given the complications with Fe-Ni redistribution, UOCs may not be appropriate samples for constraining the initial Solar System $^{60}$Fe/$^{56}$Fe ratio.

Our best approach in moving forward with $^{60}$Fe-$^{60}$Ni analyses is to make a greater effort in identifying suitable samples prior to isotope analyses. For now, it is not clear which samples have escaped late-stage, low-temperature Fe-Ni mobilization. At least 60% of chondrules from Semarkona, the least metamorphosed ordinary chondrite, show evidence for this alteration. Although this is the least amount observed for any UOC, it still indicates that the majority of these chondrules have been compromised. In situ analyses can potentially avoid extraneous Fe-Ni in chondrule fractures if samples are thoroughly characterized. Bulk analyses must also take special precaution to avoid or remove contamination. However, with the perversiveness of the remobilized Fe and Ni, this may not be possible.

Synchrotron X-ray fluorescence analyses provide the sensitivity, resolution, and efficiency for analyzing the distribution of Fe and Ni, at least in regards to Fe-Ni enrichment along chondrule fractures. Another benefit to synchrotron analyses is that they provide subsurface information of Fe and Ni distribution, which is not readily available from electron microscopy. Iron-Ni redistribution in chondrules from other chondrite groups (e.g., CO3 s) should also be investigated to determine if they could provide better constraints. Finally, synchrotron analyses of other important samples such as angrites and eucrites, which have been used to constrain the initial $^{60}$Fe/$^{56}$Fe solar system ratio, should also be carried out.

5. CONCLUSIONS

To constrain the initial $^{60}$Fe/$^{56}$Fe of the Solar System, we used the ion microprobe to measure $^{60}$Fe-$^{60}$Ni systematics in situ in chondrule olivine and pyroxene in unequilibrated ordinary chondrites (UOCs). Most chondrules do not have resolved excesses in $^{60}$Ni. Four chondrules show clearly resolved excesses in $^{60}$Ni, but they do not correlate well with the Fe/Ni ratios as expected for a closed system and the initial $^{60}$Fe/$^{56}$Fe ratios are poorly constrained (Table 1; Figs. 5 and 6). We use the excesses in $^{60}$Ni determined from some our analyses to infer a lower limit of $5 \times 10^{-8}$ for the initial $^{60}$Fe/$^{56}$Fe ratio of the region where UOC chondrules formed (Fig. 7). The upper limit is more difficult to constrain due to complications from Fe-Ni redistribution, but we infer a value of $3.0 \times 10^{-7}$ based on the upper limit of the sum of the probability distributions of each chondrule (Fig. 8). Initial $^{60}$Fe/$^{56}$Fe ratios for UOCs between $5 \times 10^{-8}$ and $3.0 \times 10^{-7}$ are inconsistent with bulk analyses, which infer initial ratios of $< 3 \times 10^{-8}$ for UOC chondrules. The initial Solar System $^{60}$Fe/$^{56}$Fe ratio of $(0.8–5) \times 10^{-7}$ inferred from this study does not necessarily require a late supernova source for $^{60}$Fe. Self-enrichment of the molecular cloud is another possible mechanism for incorporating $^{60}$Fe in the solar system. Discrepancies between bulk and in situ analyses remain, but they likely stem from late-stage open-system Fe-Ni mobilization.

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APPENDIX A. SUPPLEMENTARY MATERIAL

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REFERENCES


