Mobility of Iron and Nickel at Low Temperatures: Implications for ^{60}Fe - ^{60}Ni Systematics of Chondrules from Unequilibrated Ordinary Chondrites

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ABSTRACT

The Fe and Ni isotopic composition of ferromagnesian silicates in chondrules from unequilibrated ordinary chondrites (UOCs) have been used to estimate the initial abundance of the short-lived radionuclide, ^{60}Fe , in the early Solar System. However, these estimates vary widely, and there are systematic discrepancies in initial $^{60}\text{Fe}/^{56}\text{Fe}$ ratios inferred from *in situ* and bulk analyses of chondrules. A possible explanation is that the Fe-Ni isotope system in UOC chondrules has not remained closed (a necessary condition for isotopic dating), and Fe and Ni have been redistributed since the chondrules formed. In order to evaluate this, we collected high-spatial-resolution X-ray fluorescence (XRF) maps of UOC chondrules to better understand the distribution and mobility of Fe and Ni at the low metamorphic temperatures of these chondrites. We used synchrotron X-ray-fluorescence microscopy to map the distribution of Fe, Ni and other elements in portions of 71 chondrules from 8 UOCs (types 3.00-3.2). The synchrotron XRF maps show clear enrichment of Fe and/or Ni in fractures ranging down to micrometer scale in chondrules from all UOCs analyzed for this study regardless of petrologic type and regardless of whether fall or find, indicating that there was significant exchange of Fe and Ni between chondrules and matrix and that the Fe-Ni system was not closed. Sixty percent of chondrules in Semarkona (LL3.00) have Fe and Ni enrichment along fractures, while 80-100% of chondrules analyzed from the other UOCs show these enrichments. Mobilization was likely a result of fluid transport of Fe and Ni during aqueous alteration on the parent body and/or during terrestrial weathering. *In situ* and bulk Fe-Ni analyses that incorporate extraneous Fe and Ni from chondrule fractures will result in lowering the inferred initial $^{60}\text{Fe}/^{56}\text{Fe}$ ratios.

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1. INTRODUCTION

Iron-60 is a short-lived radionuclide that is produced efficiently only by stellar nucleosynthesis. Its former presence in the Solar System has been inferred through excesses in the daughter isotope, ^{60}Ni , that correlate with Fe/Ni in various meteorites (e.g., Shukolyukov and Lugmair, 1993a; Tachibana et al., 2006; Tang and Dauphas, 2012; Mishra and Goswami, 2014). An initial abundance of ^{60}Fe above galactic background implies that material synthesized in one or more stars that died just before the Solar System formed (e.g., supernovae) was incorporated into the early Solar System. A precise measurement of the initial Solar System $^{60}\text{Fe}/^{56}\text{Fe}$ ratio, $(^{60}\text{Fe}/^{56}\text{Fe})_{\text{SS}}$, could help identify the environment in which the Solar System formed, such as in an area of cluster star formation like Orion or in relative isolation like in Taurus Auriga (Hester and Desch, 2005). Additionally, the rapid decay rate of ^{60}Fe ($t_{1/2} = 2.6$ Myr; Rugel et al., 2009) potentially makes it a useful tool for dating early Solar System processes that fractionate Fe and Ni, such as chondrule formation, aqueous alteration, magmatic differentiation, and core formation. Since Fe is a major element in many meteoritic components, the ^{60}Fe - ^{60}Ni system can potentially be used for dating objects that cannot be easily dated by other methods (e.g., chondrule ferromagnesian silicates and sulfides).

A well-constrained $(^{60}\text{Fe}/^{56}\text{Fe})_{\text{SS}}$ is necessary in order to use the ^{60}Fe - ^{60}Ni system to determine the stellar source of short-lived radionuclides or to use it for early Solar System chronology. It is also important for thermal models of planetesimals (e.g., Moscovitz and Gaidos, 2011; Henke et al., 2012; 2013; Monnereau et al., 2013; Mare et al., 2014) because the rapid decay of ^{60}Fe is thought to generate significant internal heat (Moscovitz and Gaidos, 2011). To determine $(^{60}\text{Fe}/^{56}\text{Fe})_{\text{SS}}$, it is critical to identify materials for measurement that recorded the abundance of ^{60}Fe when they formed and have remained unaltered since that time. Components of primitive chondrites (e.g., chondrules, sulfides, and magnetite) are attractive targets because they formed early in Solar System history and have experienced relatively little thermal processing (e.g., Tachibana et al., 2006; Tang and Dauphas, 2012). Achondrites, such as angrites, have also been used to constrain the initial $^{60}\text{Fe}/^{56}\text{Fe}$ ratio of the solar system (e.g., Dauphas et al., 2008; Quitté et al., 2011) because some of them formed early (e.g., Kleine et al., 2009) and also experienced little thermal metamorphism since their formation (e.g., Mittlefehldt et al., 2002).

Ferromagnesian silicates in chondrules from unequilibrated ordinary chondrites (UOCs) have been used to constrain $(^{60}\text{Fe}/^{56}\text{Fe})_{\text{SS}}$ because: 1) the silicates (particularly pyroxenes) are relatively resistant to metamorphism and aqueous processing, 2) Fe-rich pyroxenes have high Fe/Ni ratios, and 3) chondrules in UOCs have been dated to 1-3 Myr after calcium-aluminum rich inclusions (CAIs), the first solids to form in the Solar System (Kita and Ushikubo, 2012, Connelly et al., 2012).

In situ and bulk methods have been used to measure ^{60}Fe - ^{60}Ni systematics of UOC chondrules. *In situ* methods, such as secondary ion mass spectrometry (SIMS), also known as the ion microprobe, measure chondrules in polished thick and thin sections, keeping the petrographic context intact. This method produces an internal isochron, which is constructed from the Fe/Ni ratio and Ni isotopic composition of each measured spot. The Fe/Ni ratios and excesses in ^{60}Ni should correlate positively on an isochron diagram (e.g., $^{60}\text{Ni}/^{62}\text{Ni}$ vs. $^{56}\text{Fe}/^{62}\text{Ni}$) for an undisturbed chondrule. In an undisturbed chondrule, the slope of the isochron would give the initial $^{60}\text{Fe}/^{56}\text{Fe}$ ratio for that chondrule, $(^{60}\text{Fe}/^{56}\text{Fe})_0$, and the intercept would give the initial $^{60}\text{Ni}/^{61}\text{Ni}$ ratio. The $(^{60}\text{Fe}/^{56}\text{Fe})_{\text{SS}}$ can be constrained from the chondrule $(^{60}\text{Fe}/^{56}\text{Fe})_0$ ratios using

the radioactive decay law ($N_0 = N_{ss}e^{-\lambda t}$, where t and λ are for the time and decay constant, respectively) and the UOC chondrule ages from ^{207}Pb - ^{206}Pb and ^{26}Al - ^{26}Mg chronometers. *In situ* Fe and Ni isotopic measurements of UOC chondrules show that a few chondrules have resolved ^{60}Ni excesses that correspond to $(^{60}\text{Fe}/^{56}\text{Fe})_0$ ratios ranging from 1×10^{-7} (Telus et al., 2012) to 1×10^{-6} (Mishra and Goswami, 2014). However, the isochron diagrams for these chondrules show weak correlations between excesses in ^{60}Ni and the Fe/Ni ratios. The presence of ^{60}Fe at these abundances in the early Solar System are higher than estimates for the galactic background, implying that a dying star, likely a supernova, was the source of ^{60}Fe and possibly other short-lived radionuclides (Hester and Desch, 2005; Huss et al., 2009; Ouellette et al., 2009).

Bulk techniques, such as thermal ionization mass spectrometry (TIMS) or inductively coupled plasma mass spectrometry (ICPMS) measure purified Fe and Ni extracted from dissolved chondrules. These measurements can be used to construct a “whole-rock” isochron, where each chondrule is a point on the isochron. The assumption with a whole-rock isochron is that all measured samples formed at the same time from the same initial material. If this assumption is valid, the whole-rock isochron gives the $^{60}\text{Fe}/^{56}\text{Fe}$ ratio at the time the chondrules formed. Again, the $(^{60}\text{Fe}/^{56}\text{Fe})_{ss}$ is constrained from the $(^{60}\text{Fe}/^{56}\text{Fe})_0$ ratios of the chondrules using the radioactive decay law and the chondrule ages. Bulk TIMS and MC-ICPMS measurements of UOC chondrules are consistent with $(^{60}\text{Fe}/^{56}\text{Fe})_0 < 3 \times 10^{-8}$ (Spivak-Birndorf et al., 2012a,b; Tang and Dauphas, 2012; Chen et al., 2013; Tang and Dauphas, 2015), at least an order of magnitude lower than values inferred from some SIMS data, indicating that the source of ^{60}Fe is likely from galactic background instead of a recent injection from a nearby stellar source.

Both *in situ* and bulk measurements of UOC chondrules assume that ^{60}Fe was distributed homogeneously in the solar nebula and that the Fe-Ni system remained closed since chondrule formation. One possible explanation for the poorly correlated *in situ* data and the discrepancies between *in situ* and bulk chondrule data is that our assumption of closure of the Fe-Ni isotopic system is incorrect. In order to evaluate whether the Fe-Ni system remained closed in UOC chondrules, we need to better understand the distribution and mobility of Fe and Ni at the low metamorphic temperatures (peak temperatures $< 450^\circ\text{C}$) experienced by UOCs. Here, we present results from synchrotron X-ray fluorescence (XRF) mapping of Fe, Ni and other elements in chondrules from very primitive UOCs. The synchrotron provides the sensitivity and spatial resolution necessary to rapidly map abundances of trace elements (e.g., Ni in olivine and pyroxene) at large scales (e.g., Dyl et al., 2014). Our results show that chondrules from UOCs have been severely affected by low-temperature Fe-Ni mobilization.

2. METHODS

2.1. Samples

We analyzed chondrules from the least metamorphosed UOCs (petrologic types 3.00 to 3.2). We analyzed witnessed falls, Semarkona (LL3.00), Bishunpur (LL3.1) and Krymka (LL3.2), which should not have been significantly affected by terrestrial weathering. We also analyzed chondrules from thin sections of Antarctic finds Queen Alexandra Range QUE97008 (L3.05), Elephant Moraine EET87735 (L3.05), EET90080 (L3.05), Meteorite Hills MET96503 (L3.1), and Thiel Mountains TIL82408 (LL3.1). Antarctic meteorites are given weathering grades of A, B, or C, to indicate minor, moderate or severe rusting, respectively. The Antarctic

meteorites we studied have all been classified as weathering grade B, except QUE97008 which has a weathering grade of A (Meteoritical Bulletin Database: <http://www.lpi.usra.edu/meteor/metbull.php>). We mapped a variety of chondrule types, including type I (Fe-poor) and II (Fe-rich) chondrules, with porphyritic (coarse-grained) and radiating/cryptocrystalline (fine-grained) textures. Most of the chondrules we analyzed are >500 μm across. Most of our samples are standard 1-inch-round glass thin sections. One sample, (DAP-1), is mounted in epoxy within a stainless steel bullet. In total, we mapped 71 UOC chondrules. Some of these chondrules were previously analyzed for ^{60}Fe - ^{60}Ni systematics by SIMS. Mineral compositions were determined using the scanning electron microscope and/or the electron microprobe at the University of Hawai'i (UH).

2.2 XRF mapping and data analysis

We collected XRF maps of UOC chondrules using both the Australian Synchrotron in Melbourne, Victoria and the Advanced Photon Source at the Argonne National Laboratory in Chicago, Illinois. The measurement conditions and data analyses are described below. The synchrotron is preferred for this task is because it can produce X-ray maps rapidly with similar spatial resolution and detection limits as the electron probe. We could map ~10 chondrules per day at the Australian Synchrotron. Additionally, the synchrotron beam does not damage the sample or epoxy and the beam goes through the entire thin section, which provides subsurface information on the FeNi distribution.

Electron probe spot analyses were done at UH to look at S distribution and to verify observations from the XRF maps. The beam conditions for the electron probe analyses are described in Section 2.2.4 and 2.3.

2.2.1 Australian Synchrotron XFM beamline

We collected X-ray maps of 70 UOC chondrules at the Australian Synchrotron XFM beamline (Paterson et al., 2011). The XFM beamline is equipped with a Maia energy-dispersive detector, a large-solid-angle, 384-detector array (Ryan et al., 2010). The detector is situated between the sample and the incident beam (Figure 1A). The samples were placed 10 mm away from the detector. The incident beam passes through a hole in the detector and passes through the sample. The sample emits fluorescent X-rays at various energies that are counted by the detector. The maps were collected during two separate sessions. The main difference between the two sessions is that the X-ray beam energy for the first session was 12.5 keV and that for the second session was 11.7 keV. These energies allowed us to resolve Ni X-rays from the elastic and inelastic scattered X-rays (i.e., Rayleigh and Compton scattering), which were at ~11-12 keV. An incident X-ray beam at these energies allows us to map the X-ray fluorescence of elements from Ca to Zn with the Maia detector (the Maia currently is not sensitive for elements with K-shell binding energies below those of Ca). At the beginning of each session, we analyzed standard metal foils (Mn, and Pt) to calibrate the X-ray energies and establish elemental quantitation. We collected low-spatial-resolution maps of each thin section for navigating to each chondrule. High-resolution maps of chondrules were collected using an incident X-ray beam focused to ~2 μm . We used various dwell times, mostly, between 31 and 63 msec. The pixel size was 2 μm . Under these conditions, the chondrule maps required ~0.5 to ~2.5 hours. This technique is beneficial for rapid large-scale mapping of elements $Z > \text{Ca}$.

GeoPIXETM spectral data processing software was used to generate quantitative elemental maps of the chondrules. GeoPIXE fits the spectra using dynamic matrix analysis that

deconvolves each spectrum according to the contributions from each element, background, scatter and pile up. Ryan (2001) provides a thorough explanation of this algorithm. This program allows us to estimate the concentrations of trace elements, even when they are small peaks on the shoulders of larger peaks (*e.g.*, Ni K α on Fe K β). Corrections for background, interferences, pileup, elastic and inelastic scatter were applied (see Ryan et al., 1990 for details). Because the synchrotron X-ray beam passes through the thin sections, the resulting maps are integrations over the entire 30- μ m thickness of the thin section.

Figure 1. Schematic illustration of the experimental setup at the Australian Synchrotron (A) and the Advanced Photon Source (B). The photodiode at the AS is used for alignment.

2.2.2 Advanced Photon Source GSECars 13IDE beamline

In another effort to resolve variations in the Ni concentration within chondrule olivine and pyroxene, we collected region-of-interest X-ray fluorescence maps at the APS GSECars (GeoSoilEnviro Consortium on Advanced Radiation Sources, University of Chicago) beamline 13-IDE. Region-of-interest maps assign X-rays of a certain energy range to certain elements. For instance, X-rays of energies between 5.673 and 6.109 keV are assigned to Mn K α . The Cr and Mn X-ray maps often appear very similar (see Figures 2, 3, and 6). This is because the Cr K β peak (5.947 keV) overlaps the region of interest for Mn. Data collection is very similar to that used at the Australian Synchrotron; the main differences are the energy resolution, configuration, and saturation of the detectors. At the APS, we used a 4-element, energy-dispersive, Vortex detector that is situated at ~ 90 degrees relative to the incident beam (Figure 1B). This geometry significantly reduces background from elastic and inelastic scattered X-rays. To further reduce background from scattered X-rays, we covered the detector with a collimator. We placed ~ 150 μ m thick piece of Al foil in front of the detector to reduce saturation of the detectors. This reduced the signal from Fe K α by a factor of 50, allowing us to push the detector closer to the sample and detect relatively more of the Ni signal. The detector set up and efforts to reduce saturation and background allowed for an increase in the spectral resolution of about a factor of 2 or 0.2 keV compared to the Australian Synchrotron.

The beam energy was set to 9 keV to maximize sensitivity to Ni. This set up allowed us to analyze elements from Cr to Ni. Dwell time was normally 50 ms, but we also used 100 ms in a few cases. Beam size and pixel size were 2 μm . The position of the detector was adjusted prior to each map to keep the count rate from Fe K α low enough so that the deadtime of the detector was below 40%. We mapped 23 chondrules with this technique; all except 1 were previously analyzed at the Australian Synchrotron. The X-ray maps from the APS were processed using Larch, an open-source spectral processing and analysis software (<http://cars.uchicago.edu/xraylarch/>). Corrections for changes in the beam intensity, deadtime, and background were applied using this software (Newville, 2013).

2.2.3 Detection Limits for Synchrotron XRF Ni Analyses

Detection limits for these analyses depend on the background levels. When the background is low 10 to 100 ppm Ni can be readily detectable. However, the detection limit for Ni in our case was not as good because of the high Fe/Ni ratios in chondrule olivine and pyroxene. The large signal from Fe increased the deadtime, broadened the peaks, and caused the Fe k β peak (7.06 keV) to significantly overlap the Ni K α peak (7.46 keV). These difficulties degraded the detection limit for Ni X-rays to $\sim$ 500 ppm, making it difficult to resolve the trace amount of Ni in chondrule olivine and pyroxene. This value for the detection limit is based on electron probe measurements of olivine and pyroxene grains that were mapped at the synchrotron. The detection limit for the electron probe measurements is 200 ppm. Nickel concentrations between 200 and 500 ppm in olivine and pyroxene grains could not be resolved from background using the XFM at both synchrotrons. However, Ni concentrations in chondrule fractures were clearly detected.

2.2.4 Sulfur Mapping using the Electron Microprobe

Since Fe and Ni are often associated with S, we collected S maps (along with Ca, Fe and Ni) for one chondrule from each Semarkona, Bishunpur, Krymka, QUE97008, and MET96503 using the JEOL JXA-8500F electron microprobe at UH with a 50 nA, 20 kV, focused beam and a dwell time of 20 msec. We could not analyze the S distribution at the synchrotron because it is outside the energy window available from our techniques.

2.3 Electron probe spot analyses

Contamination of Ni from the glass substrate was a concern for the XRF analyses. Therefore, we used the JEOL JXA-8500F electron microprobe at UH (10 μm beam at 100 nA and 20kV) to analyze the glass substrate of each thin section to determine the potential contribution of the glass substrate to the Ni X-ray signal from our synchrotron analyses. A NiO standard was used for standardizing our Ni spot analyses of the thin-section-glass substrate. We also collected Ni wavescans of the glass substrate under the same conditions. These show that Ni is below background in the glass substrate (See Supplementary Figure S1).

We used the electron probe under the same conditions to verify observations from our synchrotron analyses. We put the focused beam on chondrule fractures. However, in most cases, the analytical volume of the beam is much larger than the crack. Therefore the results do not provide reliable information regarding the exact concentration of Fe or Ni in the crack. They only provide an idea about the relative abundance of Fe or Ni in the crack compared to the glass substrate (e.g., Ni content in chondrule fractures is higher or similar to Ni content in the glass).

3. RESULTS

3.1 Iron and Ni enrichment in chondrule fractures

Calcium, Cr, Mn, Fe and Ni X-ray maps obtained using both the Australian Synchrotron (AS) and Advanced Photon Source (APS) along with BSE images for various chondrules are shown in Figures 2-10. The figures are arranged in order of the petrologic type of the host meteorite. The elemental maps have been stretched in order to make variations noticeable. Additional Fe, Ni and Cr maps can be found in the supplementary online material.

Semarkona (LL3.00), the least metamorphosed UOC in our collections, shows clear evidence for Fe-Ni mobilization in 60% of the chondrules studied. Semarkona is a witnessed fall and so has not experienced significant terrestrial weathering. Figure 2 shows a porphyritic pyroxene chondrule with Fe and Ni concentrated in fine fractures throughout the pyroxene grains. Many porphyritic chondrules from Semarkona show no obvious signs of Fe-Ni enrichment along chondrule fractures. For those that do, Fe-Ni enrichment is limited to discrete small regions that do not stretch across the entire chondrule (Supplementary Figure S2-S4). The most extensively altered Semarkona chondrule is a bleached radiating-pyroxene chondrule (Figure 3).

QUE97008 (L3.05) is an Antarctic find of weathering grade A. Again, Fe and Ni are enriched along fine fractures in olivine and pyroxene grains (Figure 4). The Fe and Ni concentrations appear to decrease with distance from the edge of the chondrule, indicating that the matrix is the source of Fe and Ni in the fractures. With the exception of one barred chondrule, all chondrules studied, whether porphyritic or radiating/cryptocrystalline, show extensive mobilization of Fe and Ni. EET87735 (L3.05), EET90080 (L3.05), MET96503 (L3.1) and TIL82408 (LL3.1) are Antarctic finds of weathering grade B. All chondrules studied from these chondrites show extensive evidence of Fe and Ni mobilization, with Fe and Ni enrichments along cracks permeating the mineral grains at all scales (e.g., Figure 5-7). Again, the matrix appears to be the source of Fe and Ni in the chondrule fractures.

In Bishunpur (LL3.1), a witnessed fall, porphyritic chondrules show limited enrichments of Fe and Ni along chondrule fractures (Figure 8), but the degree of alteration is definitely more extensive than that in Semarkona. We analyzed two radiating/cryptocrystalline chondrules from Bishunpur, and they both show evidence for extensive Fe-Ni mobilization (e.g., Figure 9 and Supplementary Figure S5). Among the Bishunpur chondrules studied, three showed no obvious signs of Fe-Ni mobilization.

Every chondrule that we analyzed from Krymka shows clear evidence for Fe-Ni mobilization that is often more extensive than Bishunpur chondrules, but less extensive than chondrules from Antarctic meteorites. Alteration for radiating/cryptocrystalline chondrules (e.g., Figure 10) is often more extensive than that for porphyritic chondrules (Supplementary Figure S6-S8).

Table 1 lists all the meteorites analyzed for this study and the percentage of chondrules from each chondrite that show clear evidence for Fe and Ni enrichment along chondrule fractures. Synchrotron XRF maps show clear enrichments of Fe and Ni in chondrule fractures from all of the meteorites analyzed for this study regardless of petrologic type (Figures 2-10; Table 1). The majority of chondrules studied in all meteorites showed enrichments of Fe and Ni in fractures. All UOCs show evidence for Fe-Ni mobilization regardless of whether they are falls or finds. Falls have less extensive alteration compared to the finds and of the various falls

analyzed, Semarkona, the least metamorphosed chondrite in this study, shows the least alteration. The extent of Fe-Ni mobilization in most of the Semarkona chondrules is minor. Twenty-seven chondrules of various types from Semarkona were analyzed. Type I (FeO-poor) chondrules appear to show more Fe-Ni mobilization than type II (Fe-rich) chondrules. However, this may be because type Is have less Fe, which means the background noise from high Fe peaks are less of an issue for type I chondrules. All bleached chondrules (4 in total) and all porphyritic olivine chondrules (5 in total) from Semarkona show evidence for Fe/Ni mobilization. Eighty percent (4 of 5) of the radial pyroxene chondrules and porphyritic olivine-pyroxene chondrules show evidence for Fe-Ni mobilization. Sixty percent (3 of 5) of cryptocrystalline chondrules and 50% of porphyritic pyroxene chondrules show evidence for Fe-Ni mobilization. There are six Semarkona chondrules that have fractures, but show no evidence for Fe-Ni mobilization along the chondrule fractures. They vary widely in chondrule type. Besides the fact that porphyritic olivine chondrules are not included in this list, there does not appear to be any characteristics that distinguish these chondrules from the Semarkona chondrules that do show Fe-Ni mobilization. These observations are tabulated in supplementary Table S1.

The high concentrations of Fe and Ni in the chondrule fractures were confirmed for several chondrules with electron probe spot analyses along the cracks. Some of the FeNi-enriched fractures are clearly filled with FeNi-oxides, while others may be FeNi-hydroxides based on low analytical totals. The FeO and NiO concentrations inferred from electron microprobe measurements of cracks (>1 wt% and >0.3 wt%, respectively) cannot be from the glass substrate, which has < 2000 ppm and <100 ppm Fe and Ni, respectively. Again, the results for the Fe and Ni content in the cracks are not accurate because the analytical volume of the beam is much larger than the cracks. This simply tells us that the Fe and Ni content in the chondrule fractures are much larger than in the glass substrate.

Figure 2. Backscattered-electron (BSE) image and elemental maps for a type I porphyritic pyroxene chondrule from Semarkona (SMK312B chH) obtained at the APS (ol: olivine, px: pyroxene, fs: feldspar, and sf: sulfide). The X-ray maps show that Fe is concentrated in blebs and along fine fractures in the pyroxene grains. Nickel is concentrated in blebs throughout the chondrule. Nickel is also associated with fine fractures. Spectra for the regions labeled on the BSE map are shown. Chromium and Mn show minor zoning and enrichment in what appears to be relict grains. It is possible that some of the Mn signal is from overlap with Cr (see explanation in Section 2.2.2). Gradient scales are in counts per second. Variations in Ni for the regions labeled on the BSE image and Ni map are highlighted in the spectra. The signal from the Fe-rich phases should be interpreted with caution because the deadtime for these regions were very high (>75%).

Figure 3. BSE image and elemental maps for a type II radial pyroxene (px) chondrule from Semarkona (SMKMT 62231) analyzed at the APS. Nickel is mostly concentrated along fractures, euhedral silica glass laths (gl), Fe-rich veins and the Fe-rich rim. Nickel is also enriched in bleached zones along the chondrule rim (see spectrum for spot B). Chromium and Mn distributions look very similar, but there are a few differences (e.g., upper right and lower left of X-ray maps). It is possible that some of the Mn signal is from overlap with Cr (see explanation in Section 2.2.2). Gradient scales are in counts per second. Variations in Ni for the regions labeled on the BSE image are highlighted in the spectra.

Figure 4. BSE image and elemental maps of a type I porphyritic olivine-pyroxene (px: pyroxene and ol: olivine) chondrule from QUE97008 (62228) analyzed at the AS. Iron and Ni are concentrated in along the numerous fine fractures. As the Ni map shows, the Fe- and Ni-bearing fractures occur at all scales down to the smallest scale visible on the image. Iron zoning is apparent in the olivine crystals. Chromium is concentrated in pyroxene grains. Gradient scales are in counts per second. Variations in Ni for the regions labeled on the BSE image are highlighted in the spectra.

Figure 5. BSE image and elemental maps for EET87735 (chF), a type II porphyritic olivine (ol) and pyroxene (px) chondrule analyzed at the AS. Iron shows compositional zoning in both olivine and pyroxene, while Cr compositional zoning occurs only in pyroxene. This chondrule has Fe-rich veins that emanate from the matrix. This can be seen in fractures of the large olivine grain. Nickel-rich veins cut across the entire chondrule, from one side to the other. Iron and Ni are also concentrated in blebs scattered throughout the chondrule. Gradient scales are in counts per second. Spectra for the regions labeled on the BSE image are shown.

Figure 6. BSE image and elemental maps for MET96503 (62224), a type II porphyritic olivine chondrule analyzed at the APS (ol: olivine and fs: feldspar). Iron and Cr have similar zoning in the olivine grains. Nickel enrichment in the chondrule fractures is also associated with Ni-rich blebs. Nickel variation in olivine is not resolved. Iron, Cr and even Mn are also concentrated in blebs and along chondrule fractures. It is possible that some of the Mn signal is from overlap with Cr (see explanation in Section 2.2.2). Gradient scales are in counts per second. Variations in Ni for the regions labeled on the BSE image are highlighted in the spectra.

Figure 7. BSE image and elemental maps for TIL82408 (chB), a type I porphyritic pyroxene chondrule analyzed at the AS (ol: olivine, px: pyroxene, and fs: feldspar). There is extensive Fe, Ni and Ca enrichment along chondrule fractures (Ca signal from the mesostasis has been stretched to saturation in order to point out Ca in fractures). Chromium shows exsolution features in olivine, but it is homogeneous in pyroxene. Gradient scales are in counts per second. Variations in Ni for the regions labeled on the BSE image are highlighted in the spectra.

Figure 8. BSE image, SIMS data, and elemental maps for Bishunpur chondrule (BM80 ch13), a type II porphyritic olivine-pyroxene chondrule that was mapped at the AS (ol: olivine, px: pyroxene, and gl: glass). Iron and Ni enrichment can be observed along the cracks. Gradient scales are in counts per second. Black ovals in the BSE image are from ion probe analyses. SIMS spots in the Ni enriched region (e.g., 1, 2, 3 and 4) have some of the lowest Fe/Ni ratios. Spot 6t and 6 are on the same spot. Hypersthene and San Carlos pyroxene are terrestrial standards. Iron and Ni isotopes were measured using the Cameca ims 1280 ion microprobe at the University of Hawai‘i. Iron and Ni isotopes were measured as positive ions using a 6-8 nA $^{16}\text{O}^+$ beam with a 15 μm raster. The isotopes are measured simultaneously, with ^{60}Ni , ^{61}Ni , and ^{62}Ni on electron multipliers and ^{56}Fe on a Faraday cup. A mass resolving power of ~4800 was used. Isotope ratios are calculated from the total counts acquired for each isotope during the run. Corrections were applied for detector drift, background, and deadtime. Instrumental mass fractionation was corrected internally for each individual measurement.

Figure 9. BSE image and elemental maps for Bishunpur (BM23 ch13), a type II bleached radial pyroxene (px) chondrule analyzed at the AS. Nickel is enriched along chondrule fractures. The Ni concentration in the fractures decreases with increasing distance from Fe-rich phases within the chondrule. Calcium and Cr appear to be correlated. Chromium is also enriched in the rim and Fe is enriched in sulfide blebs. Gradient scales are in counts per second. Variations in Ni for the regions labeled on the BSE image are highlighted in the spectra. Black ovals in the X-ray maps are from ion probe analyses.

Figure 10. BSE image and elemental maps for Krymka chondrule (KRM94 ch1), a type II cryptocrystalline pyroxene (px) chondrule that was analyzed at the AS. Iron and Ni enrichment can be observed along the cracks. Iron and Ca are enriched in the bleached rim. Gradient scales are in counts per second. Variations in Ni for the regions labeled on the BSE image are highlighted in the spectra. White ovals in the BSE image (black ovals in the X-ray maps) are from ion probe analyses, which may have been affected by Fe and Ni mobilization.

Table 1. Summary of synchrotron XRF mapping showing the percentage of chondrules from each UOC that show clear evidence for Fe and Ni mobilization

Chondrite	Type	Fall/Find & Year¹	Total # of chondrules analyzed	% that show Fe and/or Ni mobilization
Semarkona	LL3.00	Fall, 1940	27	60
QUE97008	L3.05	Find, 1997	8	88
EET87735	L3.05	Find, 1987	2	100
EET90080	L3.05	Find, 1990	3	100
MET96503	L3.1	Find, 1996	5	100
TIL82408	LL3.1	Find, 1982	1	100
Bishunpur	LL3.1	Fall, 1985	14	79
Krymka	LL3.2	Fall, 1946	11	100

¹Meteoritical Bulletin Database (<http://www.lpi.usra.edu/meteor/metbull.php>)

3.2 Sulfur enrichment in chondrule fractures

There appears to be a correlation between S concentration in the chondrule fractures and extent of Fe-Ni mobilization; however, more chondrules need to be analyzed to confirm this. Semarkona, QUE97008, and Bishunpur chondrules show no evidence for S associated with the Fe and Ni in the fractures (e.g., Supplementary Figures S9). However, Krymka, MET96503, and TIL82408 chondrules have S concentrated, as well as Ca, in the fractures along with Fe and Ni, (Figure 11; Supplementary Figures S10-12).

Figure 11. BSE image and S, Fe and Ni elemental maps for a chondrule from MET96503 (same chondrule as shown in Figure 6) collected using the electron microprobe. Sulfur is associated with Fe-Ni rich extraneous material in chondrule fractures. See supplementary figures for additional maps.

4. DISCUSSION

Although the concentration of Ni in chondrule olivine and pyroxene is often below the detection limit, our synchrotron analyses provide important insight into the mobility of Fe and Ni in UOC chondrules. Our main observation is of Fe and Ni enrichment along chondrule fractures in UOCs regardless of petrologic type and regardless of whether fall or find (Table 1; Figures 2-10). In some cases, Fe and Ni enrichment in chondrule fractures appears to decrease with increasing distance from the matrix (e.g., Figures 4 and 6), indicating open system Fe-Ni exchange between chondrules and surrounding matrix. These observations provide substantial evidence for pervasive late-stage redistribution of Fe and Ni in UOC chondrules. Late stage redistribution of Fe and Ni is a possible cause for the poor correlation between excess ^{60}Ni and

the Fe/Ni ratios of many *in situ* analyses and the discrepancies between *in situ* and bulk analyses, as we will discuss below.

4.1 Mechanisms for redistribution of Fe and Ni in UOC chondrites

There are various mechanisms for Fe-Ni mobilization in chondrules, including lattice diffusion, grain boundary diffusion, and fluid transport. Lattice diffusion involves redistribution of Fe and Ni through vacancies in the crystal lattice. The Ni concentration in chondrule silicates is at the trace level, olivine typically < 500 ppm and pyroxene typically < 200 ppm, making it difficult to assess the influence of lattice diffusion on the Ni distribution in these phases. Although Ni concentrations are too low to map Ni in olivine, Cr concentrations are high enough to analyze. Experimental diffusion studies of Cr in olivine and orthopyroxene indicate that Cr is essentially immobile in these phases below ~400 °C (Ito and Ganguly, 2006; Ganguly et al., 2007). The Ni diffusion rate in olivine is similar to the Fe-Mg interdiffusion rate and approximately 3 times faster than diffusion of Cr at temperatures below 700 °C (Petry et al., 2004; Chakraborty, 2010). Grossman and Brearley (2005), show that Cr begins to diffuse out of Fe-rich olivine and form chromite grains in type 3.05 chondrites and has mostly left olivine in type 3.1 chondrites. Since Ni diffuses faster than Cr in olivine, prolonged thermal metamorphism can potentially cause Ni diffusion out of olivine and concentrate it in Ni-rich metal and/or sulfide inclusions. Our Fe-Ni ion probe analyses focus on pyroxene instead of olivine because pyroxene generally has higher Fe/Ni ratios than olivine and should be more resistant to metamorphism. The Fe-Mg interdiffusion in Fe-rich orthopyroxene at 700 °C is slower by a factor of ~2.5 compared to olivine (Cherniak and Dimanov, 2010) and Cr diffusion in orthopyroxene at that temperature is slower than in olivine by a factor of ~2 (Ganguly et al., 2007; Cherniak and Dimanov, 2010). Although, experimental data for Ni diffusion in pyroxene is lacking, we expect lattice diffusion of Ni in pyroxene is slower than in olivine by a factor of 2-3 and therefore not significantly affected by thermal metamorphism at the peak temperatures of type 3.00 – 3.2 UOCs (200-400 °C; e.g., Huss and Lewis, 1994).

Grain boundaries and defects in a crystal function as short-circuit diffusion paths, producing another possible mode of redistributing elements in UOCs. In the presence of a fluid phase, grain boundary diffusion can be orders of magnitude faster than lattice diffusion (e.g., Klinger and Rabkin, 1999). Thus, diffusion along grain boundaries and cracks could potentially allow Fe and Ni to move large distances (>100 µm) into and out of olivine and pyroxene grains on a relatively short timescale. This diffusion mechanism is consistent with the observation of Fe and Ni enrichment along chondrule fractures from our XRF maps. Currently, there are no studies of grain boundary diffusion of Ni under the conditions relevant to the thermal and/or aqueous processing experienced by UOC chondrules on their parent bodies. Various mechanisms for grain boundary diffusion are discussed in Dohmen and Milke (2010). The mechanism that is the most relevant to UOC chondrules based on our observations is the structural-inhomogeneity model, also called pipe diffusion (Klinger and Rabkin, 1999). This model involves diffusion along dislocations (e.g., fractures), subgrains (e.g., inclusions), and/or lamellar precipitates. Our observations are consistent with the scenario where temperatures within chondrules are low such that lattice diffusion is negligible and diffusion occurs mainly along grain boundaries without much leakage to the adjacent crystals (referred to as type C kinetics). Mishin and Herzig (1999) provide a detailed explanation of grain boundary diffusion and the different regimes that vary with temperature and annealing times.

During fluid transport, elements are mobilized through dissolution and precipitation of minerals. FeNi-oxides and FeNi-hydroxides in chondrule fractures could have precipitated from fluid flowing through empty fractures. Fluid transport on UOC chondrite parent bodies has been inferred from the presence of hydrous phases (e.g., phyllosilicates), precipitates (e.g., calcite), and bleached chondrules. The mechanism for fluid transport was mostly likely melting of accreted ices during thermal metamorphism (e.g., Alexander et al., 2012) and/or impacts on the asteroid parent body (e.g., Bland et al., 2014). Bleached chondrules are prevalent throughout UOCs and provide substantial evidence for Fe-Ni mobilization during aqueous alteration (e.g., Figure 3). These radial or cryptocrystalline chondrules are readily recognized by porous zones, usually located along the chondrule rim, where mesostasis has been removed. Grossman et al. (2000) carried out an extensive study on the petrological, chemical, mineralogical and H-isotopic composition of bleached chondrules from Semarkona. They observed that bleached zones occur near the chondrule surface or along cracks in the chondrule. They found increases in Fe in the outer zone, the outermost region of a bleached chondrule. Bleached regions are depleted in Na and Al. Sulfur is found in sulfide blebs and stringers located throughout these chondrules, but in the bleached zone, there is some Fe, Na and Al enrichment associated with sulfide blebs and stringers. Bleached zones are enriched in H, Cl and F and their H-isotopic compositions are intermediate between compositions for the unbleached core of the chondrule and the matrix. The Grossman et al. (2000) analyses show that the bleached zones contain an abundance of Fe-rich smectite that are platy in appearance and appeared to have grown in place. Finally, the bleached zones are also rich in pentlandite, not troilite, which is found in the unbleached core of these chondrules, indicating that the Ni for pentlandite formation must have come from somewhere other than the chondrule.

Overall, our synchrotron XFM observations of two bleached chondrules from Semarkona and two from Krymka are consistent with those of Grossman et al. (2000). The outer zone is enriched in Fe, Ca is enriched in the bleached zone, and Cr shows little to no variations (e.g., Figure 10 and Supplementary Figures S3, S4, S5 and S7). The bleached rim of the chondrule from Bishunpur featured in Figure 9 appears to consist of two zones, a Fe-rich inner layer and a Fe- and Ca-poor outer layer. In another bleached chondrule from Bishunpur (Supplementary Figure S5), the bleached zone has been filled with an Fe-Ni-rich phase. Our maps show that Ni is typically enriched in the bleached and outer zones (e.g., Figure 3, 9, 10 and Supplementary Figures S5, S7 & S8). In Semarkona, the most extensive Ni mobilization occurs in a bleached chondrule (Figure 3). Most of the Ni in this chondrule is associated with feathery silica glass laths. The bleached region (see spot labeled B on BSE image) shows enrichment of Ni and there is a small outer zone that is enriched in Fe and Ni (visible in the lower left region of BSE image and X-ray maps). We normally avoid these regions during SIMS analyses, so they do not necessarily affect our *in situ* analyses. However, some open spaces that could be targeted for SIMS analyses (e.g., region labeled “C” in Figure 3) are clearly compromised by extraneous Ni. Semarkona chondrules not only experienced dissolution of the mesostasis, but there is also evidence for dissolution of Fe-Ni-rich blebs or nodules (Figure 12), which could have been the source of some of the extraneous Fe and Ni in chondrules. Grossman et al. (2000) concluded that bleaching occurred during fluid transport through the porous matrix and cracks on the parent body. Since Ni mobilization is also associated with bleaching, this lends support for Ni mobilization on the asteroid parent body, although the possibility of mobilization during terrestrial weathering remains.

Figure 12. Backscatter electron images of an Fe-rich bleb (A) and opaque nodule (B) from Semarkona chondrules (Supplementary Figure S3 and Figure 3, respectively). Porous regions within the bleb and nodule are likely due to bleaching as a result of transient fluid, which likely also mobilized Ni. The bright circular region next to Fe-rich bleb is a SIMS pit.

Constraints on the temperature during aqueous alteration are based on the thermodynamic stability of certain phases found in chondrites. For Semarkona, the least metamorphosed UOC, the presence of maghemite and the absence of hematite in chondrule rims and matrix, and the structure of smectite place an upper limit of 260°C for the temperature during aqueous alteration of these chondrites (Alexander et al., 1989). This is consistent with peak temperatures for this chondrite inferred from noble gases in presolar nanodiamonds (Huss et al., 1994), and spectroscopic features of insoluble organic matter (IOM; Cody et al., 2008). For Krymka (LL3.2), the most metamorphosed UOC analyzed in this study, peak temperatures inferred from presolar grains and the IOM indicate aqueous alteration occurred at temperatures below 400°C (Huss et al., 1994; Cody et al., 2008). The evidence from our synchrotron analyses of Fe-Ni mobilization in these chondrites and the association of Fe-Ni mobilization with bleached chondrules indicates that Fe-Ni mobilization on the parent bodies occurs at temperatures of 260°C or lower.

Terrestrial weathering is another possible mechanism for Fe and Ni enrichment along chondrule fractures (e.g., Lee and Bland, 2004). However, it can be difficult to distinguish between terrestrial weathering and parent body aqueous alteration because both (especially for Antarctic meteorites) involve fluid transport at low temperatures. All chondrules from Antarctic finds (except one chondrule from QUE97008) show clear evidence for Fe-Ni enrichment along fractures (Table 1). In particular, TIL82408 and MET96503 chondrules (Figure 7, 11 Supplementary Figures S11-S12) show enrichment of Ca and S, along with Fe and Ni, along the chondrule fractures. This may be indicative of Ca-sulfate (gypsum) formation, during terrestrial weathering (e.g., Gooding, 1986). Antarctic finds show more evidence of Fe and Ni mobilization than the witnessed falls, but not all of the finds show the same degree of alteration. For instance, QUE97008 (weathering grade A) is much less altered than MET96503 and TIL82408 (weathering grade B). Terrestrial weathering can potentially affect falls as well (e.g., Consolmagno et al., 1999). Krymka chondrules also show some enrichment of Ca and S in the chondrule fracture (Figure S10). Chondrites that have longer terrestrial residence times should have more alteration. However, we see that Semarkona and Krymka, which have similar residence times, have different degrees of alteration (Table 1).

Our observations of Fe-Ni enrichment regardless of petrologic type and regardless of whether fall or find indicate that the mechanism for Fe-Ni mobilization includes both low

temperature parent body aqueous alteration and terrestrial weathering.

4.2 Effects of Fe and Ni redistribution on ^{60}Fe - ^{60}Ni systematics

For *in situ* analyses, redistribution of Fe and Ni after the decay of ^{60}Fe affects the isochrons differently depending on whether lattice diffusion, grain boundary diffusion, or fluid transport has taken place. Grain boundary diffusion and fluid transport cause Fe-Ni exchange, with a net addition of Fe and/or Ni to chondrule olivine and pyroxene from the surrounding matrix via fractures in the chondrules. Many of the fractures are very fine and are not readily detected without the assistance of the synchrotron maps (e.g., Figures 2 and 4). *In situ* measurement spots can easily overlap fine fractures and incorporate extraneous Fe and/or Ni. The schematic isochron plot in Figure 13A illustrates the effect of extraneous Fe and/or Ni on internal isochrons. If a spot analysis incorporates pure Fe from a fracture, the Fe/Ni ratio will be higher than the true value, which will shift the point to the right on the isochron plot and will decrease the inferred initial $^{60}\text{Fe}/^{56}\text{Fe}$ ratio of the chondrule. Incorporating pure Ni with a normal isotopic composition from the fracture will change both Fe/Ni ratio and the Ni-isotope ratio such that the disturbed spot still lies along the original slope but closer to the origin. In reality, chondrule fractures contain both Fe and Ni at some level, and often the concentration of the Ni in the fractures is higher than Ni concentrations in the olivine and pyroxene. Adding both extraneous Fe and Ni in a spot analysis will change the Ni-isotope ratio and the Fe/Ni ratio (“region of possible values” for disturbed analyses is the grey region in Figure 13A), resulting in an overall decrease in the inferred initial $^{60}\text{Fe}/^{56}\text{Fe}$ ratio compared to the original value.

Metal/sulfide inclusions in chondrule olivine and pyroxene are common (e.g., Figures 2, 6, and Supplementary Figures S1-S3). They can be difficult to avoid during SIMS analyses because they are often submicron in size and are dispersed throughout the chondrule. Metal and pentlandite (Ni-rich sulfide) have low Fe/Ni ratios (e.g., $^{56}\text{Fe}/^{62}\text{Ni}$ ratios < 100) and Ni isotopic composition close to terrestrial. Troilite may have resolvable excess ^{60}Ni because the Fe/Ni ratios can be quite high (e.g., $^{56}\text{Fe}/^{62}\text{Ni}$ ratios > 1 million). During lattice diffusion, Ni isotopic exchange occurs among olivine, pyroxene and metal/sulfide, resulting in lower the Ni-isotopic ratios for Fe-silicates and moves points down on the isochron. There is also a net diffusion of Ni from olivine and pyroxene to metal/sulfide due to the partition coefficients (<http://earthref.org/KDD/>). This will preferentially remove Ni from Fe-silicates and concentrate it in sulfide/metal blebs within or adjacent to the silicates. Extracting Ni from olivine and pyroxene will increase their Fe/Ni ratios, moving points to the right on the isochron plot. SIMS spot analyses that only incorporate olivine or pyroxene where Ni isotopic exchange and Ni extraction occurred will have a higher Fe/Ni ratio and lower ^{60}Ni excesses than the undisturbed chondrule. This will result in points moving to the lower right of the isochron diagram (Figure 13B). Disturbed points (towards lower-right) have been observed and modeled in ^{26}Al - ^{26}Mg systematics of high Al/Mg phase (anorthite) and low-Al/Mg phases in a CAI from Allende, a metamorphosed chondrite (LaTourrette and Hutcheon, 1999; Ito and Messenger, 2010).

Lattice diffusion will hardly change the Fe/Ni ratio and Ni-isotopic composition of metal. If a spot analysis incorporates original metal blebs, this will move the point towards the intercept on the isochron. Sulfides are more complicated because they can be primary or secondary phases. Primary Troilite in UOCs is usually Ni-poor and has Fe/Ni ratios similar to or higher than silicates (Tachibana et al., 2003; Mostefaoui et al., 2005), while secondary sulfide is Ni-rich (pentlandite) and has low Fe/Ni ratios. Spot analyses that incorporate primary sulfide blebs may not affect the isochron significantly. However, spot analyses that overlap secondary Ni-rich

sulfide inclusions that contain Ni extracted from the bulk silicate will have a lower Fe/Ni ratio and larger excesses of ^{60}Ni than expected from the isochron; they would plot to the left of the isochron (Figure 13B). Altogether, lattice diffusion will result in a poor correlation between the Ni isotopic composition and the Fe/Ni ratio.

Figure 13. Schematic diagram illustrating the region of possible $^{60}\text{Ni}/^{62}\text{Ni}$ and $^{56}\text{Fe}/^{62}\text{Ni}$ ratios for chondrule spot analyses affected by Fe and/or Ni enriched fractures from grain boundary diffusion (A), and Ni exchange from silicates into metal/sulfide inclusions during lattice diffusion (B). Error bars have been drawn to illustrate the effect of redistribution on our ability to resolve excesses in ^{60}Ni .

Bulk Fe-Ni analyses of chondrules can be influenced by fluid transport of Fe and Ni. Extraneous Fe and Ni in bulk meteorites are usually attributed to contamination from terrestrial weathering. However, mobilization of Fe and Ni through late-stage low-temperature aqueous processing on the ordinary chondrite parent body also occurred, as discussed above. Both terrestrial contamination and parent body aqueous alteration involve fluid transport of Fe and/or Ni and can result in Fe and/or Ni enrichment along chondrule fractures and void spaces. Figure 14A shows that during fluid transport the chondrule as a whole will gain Fe and/or Ni, changing both the Ni-isotope composition and the Fe/Ni ratio, and resulting in a lower inferred initial $^{60}\text{Fe}/^{56}\text{Fe}$ ratio for the chondrule.

A common approach for removing extraneous material in chondrule fractures and pore spaces is to wash the chondrules with a mild acid, usually ethanol and HCl, prior to dissolving them for wet chemistry. Some bulk studies wash the chondrule before crushing (e.g., Tang and Dauphas, 2012), which removes surface contaminants. Other studies wash after crushing the chondrule (e.g., Chen and Papanastassiou, 2013) to remove surface contaminants and sulfides, but this also has the potential to leach Fe and Ni from the chondrule. Quitté et al., (2011) provide a detailed discussion of the effect of washing procedures on Fe-Ni systematics. They found that washing 150 mg of Bouvante (eucrite) in acetone for 5 minutes in an ultrasonic bath leached over 30% of the total Ni. If leaching removes any of the original Fe and Ni from the chondrule, or fails to remove all of the extraneous Fe and Ni, the resulting isotopic measurement will not be accurate (e.g., Figure 14B). If Ni is more readily leached than Fe (Quitté et al., 2011), this will

preferentially move the data point to right on the isochron diagram, resulting in lower initial $^{60}\text{Fe}/^{56}\text{Fe}$ ratios.

Lattice diffusion can also affect bulk isochrons if the temperatures are sufficiently high. Since we could not resolve Ni variations in olivine and pyroxene due to limitations of detection, our synchrotron analyses cannot be used to address lattice diffusion issues. Nevertheless, bulk analyses of eucrites (metamorphosed achondrites) indicate lattice diffusion of Ni may have occurred. Quitté et al., (2011) analyzed mineral separates and bulk samples of the eucrite, Juvinas, and found that metal and chromite data plot to the left of the regression line for the bulk isochron, while the pyroxene data plot to the right of the bulk isochron. They attributed the disturbed eucrite isochron to redistribution of Ni from pyroxenes into the metal and chromite during thermal metamorphism. Although we do not expect such extensive diffusion at the temperatures of UOCs, the ^{60}Fe - ^{60}Ni systematics of Juvinas from Quitté et al. (2011) are consistent with what we expect for the effect of lattice diffusion on the internal isochrons.

Figure 14. These diagrams illustrate the region of possible $^{60}\text{Ni}/^{58}\text{Ni}$ and $^{56}\text{Fe}/^{58}\text{Ni}$ ratios for bulk chondrule analyses affected by Fe and/or Ni enriched fractures from grain boundary diffusion (A), and Fe and Ni extraction from the chondrule during leaching (B). Error bars have been drawn to illustrate the effect of redistribution on our ability to resolve excesses in ^{60}Ni .

4.3 Implications for ^{60}Fe - ^{60}Ni analyses of UOC chondrules and other meteorite samples

Low-temperature mobilization of Fe and Ni in chondrules from type 3.00 – 3.2 UOCs calls into question whether these are actually the appropriate samples for constraining the initial $^{60}\text{Fe}/^{56}\text{Fe}$ ratio of the Solar System. Appropriate samples must have remained closed systems since the chondrules formed in order for the derived date to be relevant to chondrule formation, the event that can be dated by the Pb-Pb system and other isotopic techniques. Our observations show that most chondrules from type 3.0-3.2 UOCs have experienced open-system exchange of Fe and Ni, either on the parent body or on Earth, or both.

Ion probe analyses of UOC chondrules have been of both falls and finds. There are discrepancies between SIMS analyses from different groups. Mishra and Goswami (2014) and Mishra and Chaussidon (2014) found evidence for ^{60}Fe in many UOC chondrules with initial $^{60}\text{Fe}/^{56}\text{Fe}$ ratios ranging from 2×10^{-7} to 1×10^{-6} , whereas Telus et al. (2012) found that very few chondrules show clear evidence for ^{60}Fe , with those that do giving initial ratios of 1×10^{-7} to

3×10^{-7} . The source of inconsistencies from different SIMS groups is still unclear. Some of our SIMS analyses clearly overlap Fe-Ni rich fractures within the chondrules (e.g., Figures 8 and 10). The work presented here indicates that this overlap can explain the poor correlation between excess ^{60}Ni and the Fe/Ni ratios of many of the SIMS analyses (e.g., Telus et al., 2012). The chondrule featured in Figure 8 was analyzed with the SIMS prior to collecting the elemental maps at the synchrotron. SIMS spots 1 through 4 clearly overlap a region enriched in extraneous Ni. These spots also have some of the lowest Fe/Ni ratios. However, not all of the spots with low Fe/Ni ratio or low Ni-isotope ratios are obviously affected by extraneous Ni, such as spots 9, 10 and 11. Eliminating points that have been clearly contaminated does not improve the correlation between the Fe/Ni and Ni-isotope ratios. Chondrules that do not show resolved excess ^{60}Ni , despite high Fe/Ni ratios (e.g., Figure 10), may have experienced extensive redistribution of Fe and Ni. We save detailed discussion of the SIMS data for a future publication.

Bulk Fe-Ni analyses of UOC chondrules from falls and finds infer initial ratios $< 3 \times 10^{-8}$ (Spivak-Birndorf et al., 2012a,b; Tang and Dauphas, 2012; Chen et al., 2013; Tang and Dauphas, 2015), 1-2 orders of magnitude lower than what is inferred from SIMS analyses. In order to avoid being compromised by extraneous material in chondrule fractures, the chondrules are washed in weak acids prior to analyses. Although washing chondrules helps with removing surficial material, it is not clear how effective this is for removing material in fine fractures. If washing does not remove all extraneous material in chondrule fractures, the extra Fe and Ni will generate erroneously lower initial ratios (Figure 14B). Prolonged washing in acid may leach Fe and Ni from silicates, which can also compromise these analyses. Given the prevalence of Fe-Ni enrichment in UOC chondrules, it is likely that these analyses have been compromised by Fe-Ni mobility.

Identifying UOC chondrules with unaltered ^{60}Fe - ^{60}Ni systematics requires thoroughly characterizing each chondrule via electron probe or synchrotron mapping prior to isotopic analyses. It may be impossible to find appropriate samples for bulk analyses of UOC chondrules since Fe- and Ni-enriched fracture are difficult to avoid with this technique. *In situ* analyses can potentially avoid chondrule fractures if suitable spots for analyses are identified beforehand. Based on chondrules from Semarkona, the least altered UOC, bleached chondrules and porphyritic olivine chondrule should be completely avoided because they all show evidence for Fe-Ni mobilization (Supplementary Table S1). Non-bleached cryptocrystalline chondrules and porphyritic chondrules from Semarkona show the least amount of Fe-Ni mobilization. Cryptocrystalline chondrules are not particularly good for SIMS analyses because the grain sizes are too small. Based on the grain size, porphyritic pyroxene chondrules may be the best types of chondrules from UOCs to analyze; however, since 50% of these chondrules show evidence for Fe-Ni mobilization, including cracks permeating the phenocrysts at all scales, the chondrules should be characterized thoroughly for Fe and Ni mobilization prior to SIMS analyses. Other types of meteorites may potentially be better candidates for studying ^{60}Fe - ^{60}Ni systematics. However, each sample needs to be characterized in detail to determine whether Fe and Ni have remained undisturbed by solid-state diffusion, aqueous alteration, and/or terrestrial weathering.

4.4 Implications for the ^{53}Mn - ^{53}Cr system

Extensive Fe-Ni mobility in chondrules indicates that late-stage redistribution of other more-mobile elements such as Cr need to be investigated. This is especially important for ^{53}Mn - ^{53}Cr ($t_{1/2} = 3.7$ Myr) age dating. Some of our chondrules show Cr exsolution features (e.g., Figures 6 and 7). This is consistent with observations from Grossman and Brearley (2005). We

cannot say for certain whether Mn is also mobile as suggested in Figure 6 because the Cr K β peak overlaps the Mn K α peak. These observations indicate that using ^{53}Mn - ^{53}Cr to date chondrules may be problematic. If redistribution of Cr ended before ^{53}Mn completely decayed, then it is possible that ^{53}Mn - ^{53}Cr systematics of chondrules can constrain the time of Fe-Ni mobilization. If Cr mobilization occurred after ^{53}Mn completely decayed, then ^{53}Mn - ^{53}Cr systematics of chondrules may not provide reliable ages. Chromium mobilization may explain some scatter in the ^{53}Mn - ^{53}Cr ages of chondrules (Nyquist et al., 2009), but this requires a detailed investigation. Late-stage Al-Mg mobilization must also be investigated, especially since the ^{26}Al - ^{26}Mg ($t_{1/2} = 0.75$) ages are the primary constraints for chondrule ages.

5. CONCLUSIONS

Identifying samples suitable for Fe-Ni analyses is critical for constraining the initial $^{60}\text{Fe}/^{56}\text{Fe}$ ratio of the Solar System and for the continued development of the ^{60}Fe - ^{60}Ni chronometer. We have focused our Fe-Ni ion probe analyses on chondrules from UOCs in order to avoid complications from Fe-Ni redistribution. However, synchrotron X-ray fluorescence maps collected at the Australian Synchrotron and the Advanced Photon Source show substantial evidence for Fe and Ni mobilization along chondrule fractures in UOCs regardless of petrologic type or whether fall or find (Table 1, Figures 2-10). Even Semarkona, the least metamorphosed UOC chondrite, shows evidence for Fe-Ni mobilization. Our synchrotron X-ray data provides evidence for significant exchange of Fe and Ni between chondrules and matrix, which provides some explanation for the weak correlation between excess ^{60}Ni and the Fe/Ni ratios from *in situ* analyses (Figure 13) and for the discrepancies between *in situ* and bulk Fe-Ni analyses (Figure 14). Late-stage Fe-Ni mobilization was likely facilitated by fluid considering the large distances (>100 μm) that Fe and Ni have been redistributed in many chondrules. Iron-nickel redistribution on this scale requires caution in collecting and interpreting *in situ* and bulk Fe-Ni data. *In situ* analysis may still be appropriate for these analyses if chondrule fractures are avoided with a high degree of care. Otherwise, UOC chondrules may not be suitable for constraining the initial $^{60}\text{Fe}/^{56}\text{Fe}$ of the Solar System.

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