

LARGE MASS-DEPENDENT NICKEL ISOTOPE FRACTIONATION IN ORGUEIL CARBONATE: IMPLICATIONS FOR Fe-60 IN THE EARLY SOLAR SYSTEM. P. Boehnke^{1,2}, K. D. McKeegan³, T. Stephan^{1,2}, R. C. J. Steele⁴, R. Trappitsch⁵, A. M. Davis^{1,2,6}, M. J. Pellin^{1,2,6,7}, and M.-C. Liu³, ¹Department of the Geophysical Sciences, The University of Chicago, Chicago, IL, USA (pboehnke@gmail.com), ²Chicago Center for Cosmochemistry, Chicago, IL, USA, ³Department of Earth, Planetary, and Space Sciences, The University of California, Los Angeles, CA, USA, ⁴School of Earth and Environmental Sciences, University of St. Andrews, St. Andrews, UK, ⁵Lawrence Livermore National Laboratory, Nuclear and Chemical Sciences Division, Livermore, CA, USA, ⁶Enrico Fermi Institute, The University of Chicago, Chicago, IL, USA, ⁷Materials Science Division, Argonne National Laboratory, Argonne, IL, USA.

Introduction: Knowledge of the initial abundance of ^{60}Fe in the early Solar System is critical for understanding the astrophysical environment of the Sun's formation. This is because ^{60}Fe is produced only in stars and not by particle irradiation and has a relatively short half-life (2.62 My, [1]); therefore, a Solar System initial $(^{60}\text{Fe}/^{56}\text{Fe})_0$, above the galactic background is seen to require a supernova trigger for Solar System formation. For this reason, numerous investigations have sought to determine $(^{60}\text{Fe}/^{56}\text{Fe})_0$ (see [2], for a review).

High precision measurements of dissolved bulk samples of differentiated and chondritic meteorites by inductively coupled multi-collector plasma mass spectrometry (MC-ICP-MS) are in excellent agreement, and all find $(^{60}\text{Fe}/^{56}\text{Fe})_0 < 2 \times 10^{-8}$ (e.g., [3]). In contrast, in-situ analyses by secondary ion mass spectrometry (SIMS) often find ^{60}Ni excesses in mineral phases with very high Fe/Ni ratios, leading to inferences of $(^{60}\text{Fe}/^{56}\text{Fe})_0$ up to two orders of magnitude higher than the limits estimated from bulk measurements (e.g., [4,5]), which, if correct, would require an injection of supernova material within a few million years of Solar System formation.

SIMS measurements of nickel isotopes are challenging due to unresolvable isobaric interferences on ^{58}Ni by ^{58}Fe and on ^{64}Ni by ^{64}Zn . This means that SIMS nickel isotope measurements can only accurately determine relative abundances of ^{60}Ni , ^{61}Ni , and ^{62}Ni . Therefore, the standard analytical procedure is to correct the measured $^{60}\text{Ni}/^{62}\text{Ni}$ ratio with the measured $^{61}\text{Ni}/^{62}\text{Ni}$ ratio using an assumed mass fractionation law (e.g., [4,5]). However, ^{61}Ni is a minor isotope, comprising only ~1.1% of nickel resulting in measurement precision on $\delta^{61}\text{Ni}_{62}$ lower than that of $\delta^{60}\text{Ni}_{62}$, and therefore making the correction for natural mass-dependent fractionation problematic.

It is important to remember that there are two distinct phases of mass-dependent isotope fractionation, both of which need to be corrected for to accurately calculate any ^{60}Ni excess. The first occurs to the sample in nature, perhaps as a result of evaporation, condensation, or diffusion, and needs to be corrected for by measuring two additional isotopes of nickel besides

^{60}Ni (e.g., ^{61}Ni and ^{62}Ni). The second occurs during the analysis (i.e., instrumental mass-fractionation) and can be corrected for by measuring standards under similar analytical conditions. In general, an uncorrected isotopic measurement is affected by the sum of these two independent mass-fractionations, and each must be corrected for before calculating the true ^{60}Ni excess. The primary concern in this work is with natural rather than instrumental mass-dependent fractionation.

Here, we present a case study of samples that yielded apparent Fe/Ni fossil isochrons when analyzed by SIMS. We then analyzed the same samples by resonance ionization mass spectrometry (RIMS), which can also reliably measure ^{58}Ni , even in the presence of high abundances of iron. We observe significant $^{60}\text{Ni}/^{62}\text{Ni}$ ratio variability that is clearly caused by mass-dependent isotope fractionation in the sample. Our results demonstrate that natural mass-dependent isotope fractionation of nickel, not previously recognized in SIMS analyses of meteorite samples, can lead to apparent isochrons. Finally, we show that the high inferred $(^{60}\text{Fe}/^{56}\text{Fe})_0$ from SIMS measurements arises from incorrectly calculated uncertainties, particularly on the $^{61}\text{Ni}/^{62}\text{Ni}$ ratios.

Methods: The samples in this study are three breunnerite grains from the Orgueil carbonaceous chondrite. These iron- and manganese-rich carbonates are characterized by very high Mn/Cr and Fe/Ni ratios, and thus are attractive samples in which to seek evidence for in-situ decay of extinct ^{53}Mn and ^{60}Fe . $^{53}\text{Mn}/^{53}\text{Cr}$ ages measured on two (Br-25 and Br-33) of these samples show that they formed within ~5 My of Solar System origin [6].

We carried out two analytical sessions for Fe/Ni ratios and nickel isotopes using both the UCLA CAMECA *ims1270* and *ims1290* ion microprobes. In the first session, using the *ims1270*, we collected $^{56}\text{Fe}^+$, $^{57}\text{Fe}^+$, $^{60}\text{Ni}^+$, and $^{62}\text{Ni}^+$ in monocollection mode using the axial Faraday cup for iron and the axial electron multiplier for nickel. The primary beam consisted of ~3 nA of O_2^- that was focused into a ~30 μm spot. The analyses were carried out at a mass resolving power $m/\Delta m$ of ~5,000, which is sufficient to resolve most molecular mass interferences. Isotopic data were col-

lected after 120 s of presputtering to remove potential contamination from the sample surface. The second analytical session, using the *ims1290*, was nearly identical, with the only differences being collection of an additional mass, $^{58}\text{Fe}^+ + ^{58}\text{Ni}^+$, with the axial electron multiplier, a slightly more intense primary beam of ~ 5 nA of O^- , and 30 s of presputtering.

We performed RIMS analyses on the same samples using the CHicago Instrument for Laser Ionization (CHILI) [7]. Our RIMS measurements were carried out with a spatial resolution of <10 μm using a 351 nm desorption laser. The resonance ionization scheme for nickel is detailed in [7] and uses four lasers to ionize nickel atoms ablated from the sample from both the ground state and from a low-lying excited state, which contains $\sim 60\%$ of the desorbed nickel atoms [8]. We used a terrestrial siderite as our primary standard to correct for instrumental mass fractionation. San Carlos olivine was analyzed as a secondary standard and to investigate possible matrix effects. We corrected for a minor contribution of nonresonantly ionized ^{58}Fe on the ^{58}Ni peak by peak-stripping, based on the measured ^{56}Fe abundance and the Solar System $^{58}\text{Fe}/^{56}\text{Fe}$ ratio. This correction was $<10\%$ in all cases. Off-resonance analyses showed small peaks on masses 60 and 62, which we were not able to suppress and were corrected for based on the measured ^{56}Fe abundance. This correction was also small, $<10\%$ in most cases. The uncertainties in our measurements include contributions from counting statistics, background subtraction, and reproducibility of the mass fractionation correction on the standard.

Results: Our SIMS analyses of Orgueil carbonate Br-33 show an increase in $^{60}\text{Ni}/^{62}\text{Ni}$ ratio as a function of $^{56}\text{Fe}/^{62}\text{Ni}$ ratio. This is consistent with an apparent fossil isochron whose slope would imply an $^{60}\text{Fe}/^{56}\text{Fe}$ ratio of $(4.2 \pm 0.5) \times 10^{-7}$ (1σ) at the time of Br-33's formation; the correlation has a mean squared weighted deviation (MSWD) of 4.2. On the other hand, Br-25 shows an elevated but constant $^{60}\text{Ni}/^{62}\text{Ni}$ ratio as a function of $^{56}\text{Fe}/^{62}\text{Ni}$ ratio. A weighted linear regression for the Br-25 data suggests only an $^{60}\text{Fe}/^{56}\text{Fe}$ ratio of $(3 \pm 7) \times 10^{-8}$ (1σ) (MSWD = 1.1) at the time of Br-25's formation.

Our results from measuring these same carbonates using CHILI support the finding of $^{60}\text{Ni}/^{62}\text{Ni}$ ratio variability in Br-25 and Br-33. However, we observe a strong correlation of $\delta^{60}\text{Ni}_{58}$ with $\delta^{62}\text{Ni}_{58}$ that demonstrates that the $^{60}\text{Ni}/^{62}\text{Ni}$ ratio variability is entirely due to mass-dependent isotope fractionation. In two out of our three carbonates (Br-25 and Br-33), we find a large range of mass-dependent isotope fractionation of up to $\sim 35\%/\text{u}$, predominantly favoring the light isotopes. Indeed, once we internally normalized the data by cor-

recting for the natural isotope fractionation using the exponential law, they show no $\Delta^{60}\text{Ni}_{62/58}$ excesses that are resolved at the 2σ level.

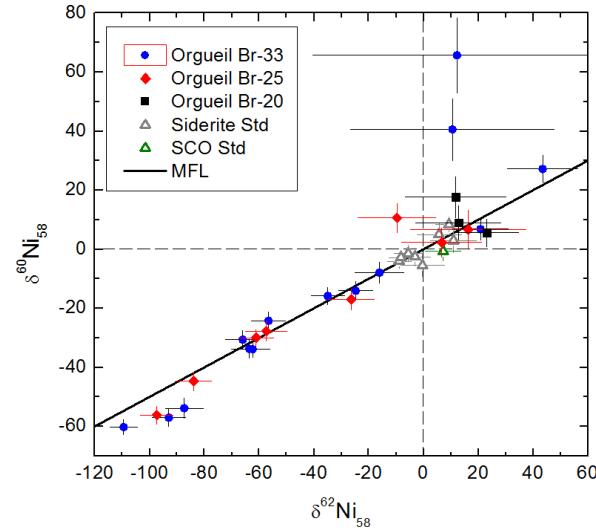


Figure 1: Ni isotopic compositions of individual spots from three Orgueil carbonates, measured using CHILI and normalized to a terrestrial siderite standard. San Carlos olivine (SCO) was measured in the same session to show the limited range of matrix effects. The line labeled "MFL" shows the line along which the measurements should plot if mass-dependent isotope fractionation has occurred. Uncertainties are 1σ .

Summary and outlook: We show that nickel isotopes in meteoritic samples, carbonates from Orgueil, can be isotopically fractionated with a range of $35\%/\text{u}$ and that SIMS cannot adequately measure mass-dependent isotope fractionation of nickel in high-Fe/Ni phases. Therefore, we conclude that any ^{60}Ni excess that is comparable to or smaller than 70% cannot be uniquely assigned to the decay of ^{60}Fe .

Next we plan to measure Fe/Ni ratios in addition to Ni isotopes using CHILI with our recently modified Ga ion gun to constrain the $(^{60}\text{Fe}/^{56}\text{Fe})_0$ of the Solar System.

References: [1] Rugel G. et al. (2009) *Phys Rev Lett*, 103, 7. [2] Elliott T. and Steele R. C. J. (2017) *Rev Mineral Geochem*, 82, 511–542. [3] Tang H. and Dauphas N. (2015) *Astrophys J*, 802, 22. [4] Mishra R. and Chaussidon M. (2014) *EPSL*, 398, 90–100. [5] Telus M. et al. (2012) *MAPS*, 47, 2013–2030 [6] Steele R. C. J. et al. (2017) *GCA*, 201, 245–259. [7] Stephan T. et al. (2016) *Int J Mass Spectrom*, 407, 1–15. [8] Trappitsch R. et al. (2018) *GCA*, 221, 87–108.

LLNL-ABS-744242