SEARCH FOR $^{60}\text{Fe}$ IN CHONDRULES FROM ALLENDE AND TIESCHITZ. G. Quitté$^1$, B. Zanda$^2$, A.N. Halliday$^3$, C. Latkoczy$^4$ and D. Günther$^5$, $^1$GMR, ETH, Sonneggstrasse 5, 8092 Zurich, Switzerland (quitté@erdw.ethz.ch), $^2$LEME, Muséum National d’Histoire Naturelle, Paris, France. $^3$Department of Earth Sciences, Oxford University, Oxford, United Kingdom, $^4$Laboratory of Inorganic Chemistry, ETH, Zurich, Switzerland.

Introduction: Chondrites are early objects composed of primitive undifferentiated material. The study of their earliest and most primitive components like the refractory inclusions (CAIs) and the chondrules provide us with strong constraints on the events in the early solar system. Chondrules are millimeter-sized spheres present in abundance in most chondrites. They are thought to have formed by melting of solid precursors and subsequent cooling in a reducing environment. Different generations of chondrules exist and two types can be distinguished: type I chondrules are volatile poor, FeO poor and metal rich, whereas type II are volatile rich, FeO rich and metal poor. The reduced type I chondrules are sometimes assumed to derive from the oxidized type II chondrules by melting and evaporative loss of Fe and Si.

The exact chronology of chondrules is poorly constrained. Some chondrules appear to have formed at the same time as CAIs according to [1,2]. Others did not form until 2 Myrs later [3-5]. Bizzarro et al. [6] suggested that chondrules began to form together with CAIs but that the process lasted 1.5 Myrs. The $^{60}\text{Fe}$/$^{60}\text{Ni}$ chronometer is a powerful tool for studying the chronology of formation of chondrules because of the very short half-life of $^{60}\text{Fe}$ ($t_{1/2} = 1.49$ Myrs). Chondrules with very different histories can be located close to each other in the same meteorite (e.g. [7]). It is therefore crucial to analyze individual chondrules rather than pooled samples. Kita et al. [4] already measured the Ni isotopic composition in the FeO-rich olivine of one type II chondrule in Semakona (LL3.0) using SIMS and detected no anomaly in $^{60}\text{Ni}$ due to the in situ decay of $^{60}\text{Fe}$. However, the precision of the SIMS measurements is about one per mil, while the expected anomaly in chondrules is smaller than a few epsilon units in most cases. We therefore decided to pursue this first work with new high precision analyses for individual chondrules. The first step of the project was to demonstrate the feasibility and validity of the technique. To do so, we chose chondrules that could be readily extracted from two chondrites: Allende and Tieschitz, even though these two meteorites may not be the best candidates to date chondrule formation because they have been altered and metamorphosed.

Samples and technique: Allende is an oxidized CV3 chondrite, partially altered and metamorphosed (metamorphic grade 3.7). Tieschitz is a H3.6 unequilibrated ordinary chondrite, slightly shocked (S1/2). In fact, it has been demonstrated that the chondrules in this meteorite have had different shock histories, some of them being unshocked, and that closely packed chondrules can be very different.

After acid digestion, nickel was separated from the matrix elements in a three-step procedure. A first ion exchange facilitated the full separation of Fe (and Zn) from Ni. Then, a liquid-liquid extraction based on the affinity of Ni for the DMG (dimethylglyoxime) allowed the separation of Ni from Cu, Al, and the other metal cations. Finally, the Ni fraction was purified on a second column filled with ion exchange resin. The whole chemical separation was adapted from [8]. The Ni isotope measurements were performed using a new large geometry and high resolution MC-ICPMS, the Nu1700 instrument installed at ETH, with a mass resolution m/Δm of about 2600 to resolve the ArNe$^+$ and ArO$^+$ interferences on masses 58 and 60. In most cases the samples were measured at least 10 times over different sessions, interspersed with standard solutions. The mass fractionation was corrected by normalizing the $^{62}\text{Ni}$/$^{58}\text{Ni}$ ratio to 0.05338858 [9] using an exponential law.

Results: The Fe/Ni ratio lies between 55 and 1240 for Tieschitz chondrules and is about 8 times more fractionated than in Allende. Because of their high Fe/Ni ratio, chondrules are expected to show an excess of radiogenic $^{60}\text{Ni}$ due to the in situ decay of $^{60}\text{Fe}$ if they formed early in the solar system history and remained undisturbed since that time. However, almost all samples present the same Ni isotopic composition as the terrestrial standard within uncertainty. Only two Tieschitz chondrules show a small but well resolved $^{60}\text{Ni}$ excess. The $\varepsilon^{60}\text{Ni}/^{59}\text{Ni}$ varies from $-0.8\pm0.7$ to $0.3\pm0.1$ for Allende and from $-0.1\pm0.2$ to $0.9\pm0.6$ for Tieschitz. There is no correlation between the isotopic composition and the Fe/Ni ratio of the samples. A SEM-EDS analysis confirmed that all Allende chondrules are of type I as expected in carbonaceous chondrites, whereas all but possibly one Tieschitz chondrules are of type II.
Discussion: Allende is a chondrite of type 3.7 [10] and Tieschitz of type 3.6. The absence of a large excess of radiogenic Ni on the one hand and the lack of correlation between the isotopic composition and the elemental ratio on the other hand could be due to thermal and aqueous alteration and metamorphic processes that may have caused redistribution of Fe and Ni. A late isotopic redistribution has already been indicated in Tieschitz by Sm-Nd and Ar-Ar measurements. More precisely, Krestina et al. [11] observed a bimodal distribution of Sm-Nd ages among Tieschitz chondrules: one subset shows formation ages of 4.55 Ga while other chondrules yield ages of about 2 Ga, interpreted as the age of aqueous alteration on the parent body [12]. Chemical exchange between chondrules and matrix or rim material under such conditions can lead to a partial re-equilibration and disturbance of the isotopic system. Our data seem compatible with this interpretation: the two chondrules with a small $^{60}$Ni excess may belong to the first subset formed whereas the other samples have been re-equilibrated much later when $^{60}$Fe was extinct. If we assume that chondrules formed from a chondritic reservoir (solar nebula or chondrule precursors of chondritic composition), the slope of the best fit line going through the chondritic point (green on the figure) and the chondrule with the largest $^{60}$Ni anomaly provides an upper limit of $3.4*10^{-7}$ for the $^{56}$Fe/$^{56}$Fe ratio at the time chondrules in Tieschitz formed. With an initial $^{56}$Fe/$^{56}$Fe value of $10^6$ for the solar system [13], we estimate that some chondrules in Tieschitz may have formed about 2.3 Myrs after CAIs. This is consistent with chronologies inferred from other chronometers. However, a value of $3.4*10^{-7}$ is significantly higher than the estimated $^{56}$Fe/$^{56}$Fe ratio at the formation time of Semarkona chondrules [4], which is surprising as Semarkona is much less metamorphosed than Tieschitz and should have preserved the original isotopic signature of chondrules. Therefore, our preliminary data for Tieschitz have to be considered with caution. It may well be that the Fe-Ni system has been disturbed in all chondrules and that no chronological interpretation can be inferred from the results.

It is well known that Ni migrates with metamorphism [14], which allows the estimation of the metamorphic temperature of pentlandite-bearing chondrites. As Tieschitz is slightly less metamorphosed than Allende, some chondrules of the former meteorite are less disturbed and kept their original isotopic composition.

Conclusion: We have demonstrated with this first study that our technique is suitable for high precision Ni isotopic measurements in individual chondrules. The two meteorites selected for this work (Allende and Tieschitz) are partially altered and metamorphosed. The Fe-Ni isotopic system has been disturbed and most samples show no excess of radiogenic $^{60}$Ni despite their high Fe/Ni ratio and early formation. The next step in this project will be to analyze chondrules from primitive, unaltered, non-metamorphosed chondrites. We will first select chondrites with a low metamorphic temperature or unequilibrated Ni in the pentlandite. Semarkona (LL3.0, metamorphic temperature = 203±20°C, compared to 314±50°C for Allende, [15]) shows no anomaly in $^{60}$Ni [4] within an uncertainty of 10 epsilon. It would be interesting to check if these chondrules still have no anomaly at the 0.3 epsilon level. Our new technique offers this possibility.