

## HIGH PRECISION NICKEL ISOTOPE MEASUREMENTS OF FE-NI METAL IN METEORITES

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**Introduction:** Nickel has five isotopes (58, 60, 61, 62 & 64) and is potentially a powerful early Solar System chronometer and tool to identify the astrophysical setting in which our Solar System formed. Variations of <sup>60</sup>Ni abundances in meteorites can result from the decay of short-lived <sup>60</sup>Fe ( $t_{1/2} = 1.49$  Myr), if it was injected by a nearby supernova into the proto-Solar System shortly before or during its creation. Furthermore, variations in the abundances of neutron-rich isotopes, <sup>62</sup>Ni and <sup>64</sup>Ni, might trace different stellar nucleosynthetic inputs into the proto-Solar System and reveal time-scales of mixing of these nucleosynthetic components in the proto-planetary disc.

Recently published Ni isotope data for meteorites has produced somewhat conflicting results [1,2,3]. No evidence for measurable Ni isotopic anomalies in Fe-Ni metal of iron meteorites was found by Quitte et al. [1]. The study of [2] also found no resolvable  $\epsilon^{60}\text{Ni}$  variations in irons and pallasites. In contrast, using somewhat higher precision techniques and different normalising isotopes to correct for instrumental mass bias, Bizzarro et al. [3] reported deficits in  $\epsilon^{60}\text{Ni}$  and  $\epsilon^{62}\text{Ni}$  in most classes of differentiated meteorites compared to Earth, Mars and chondrites. Uniform deficits in  $\epsilon^{60}\text{Ni}$  in these early formed differentiated meteorite samples led Bizzarro et al. to conclude that <sup>60</sup>Fe was injected into the Solar System ca. 1 Myr after its formation and when the planetesimals from which these meteorites originate had already accreted. <sup>62</sup>Ni deficits in the irons and pallasites were interpreted to reflect preservation of nickel nucleosynthetic anomalies on a planetesimal scale in the Solar System as has been demonstrated for Cr isotopes [3,4].

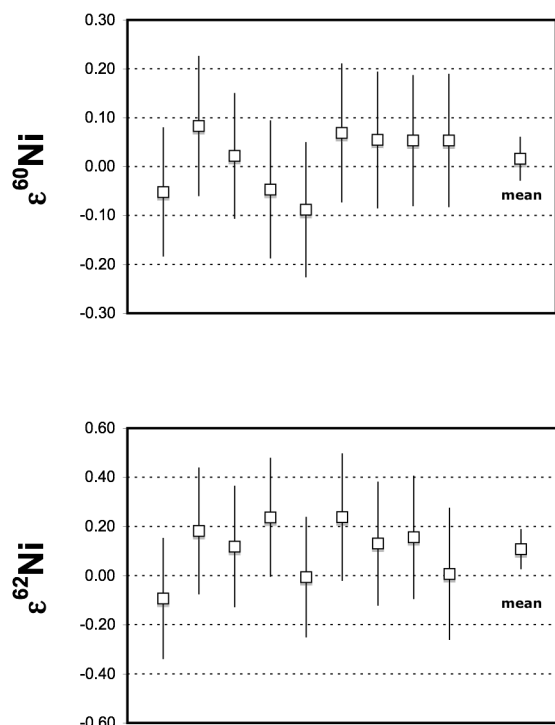
Precise and accurate measurement of Ni isotope ratios by multiple-collector inductively coupled plasma mass spectrometry (MC-ICPMS) is hampered by two factors that largely result from the small size of three of the nickel isotopes (61, 62 and 64). This makes it difficult to: (a) precisely measure ratios involving, in particular, <sup>61</sup>Ni due to both analytical noise during analyses and also the need to very precisely measure baselines; (b) be confident that small isobaric interferences do not compromise the accuracy of the Ni isotope data. Here, we describe analytical developments intended to improve MC-ICPMS techniques for precise and accurate Ni isotopic analysis and report preliminary data for Fe-Ni metal from irons and pallasites.

### Analytical Methods:

*Chemical separation of Ni.* Fe-Ni metal was digested in 6M HCl. After centrifugation, the supernatant was subjected to a two-step column chemistry on columns loaded with 4 mL of Eichrom TEVA spec resin following the methods of [3]. In the first step Ni is eluted with 6M HCl and in the second step Ni is eluted with concentrated HCl. This chemistry results in > 99% recovery of Ni and effectively separates Ni from major constituents in the Fe-Ni metal like Fe and Co. However, we note that this chemistry results in small but significant amounts of <sup>31</sup>P from the Fe-Ni metal remaining in the Ni cut. We have analysed Ni separated from pallasite metal samples Esquel and Brenham, as well as Ni cuts for Esquel, Arispe and Mundrabilla that were analysed and reported in the study of [3].

*Ni isotopic measurements by MC-ICPMS.* Ni isotope ratios were measured on a Nu Plasma MC-ICPMS at Victoria University of Wellington. The Faraday collector used to measure <sup>58</sup>Ni was equipped with a 10<sup>10</sup> Ohm resistor that allows larger 61 and 62 ion beams to be measured during analysis. Ni is introduced into the plasma via a desolvating nebuliser. Each measurement comprises 10 min of baseline acquisition and 20 min of data acquisition that is acquired in two blocks. Samples are bracketed by analyses of standards and data are reported in the epsilon or per mil notation as the difference from the average values of the two bracketing standards. Uncertainties on each analysis are calculated by incorporating that on the sample run with those from the bracketing standards. Our preferred normalisation scheme uses the <sup>61</sup>Ni/<sup>58</sup>Ni ratio to correct for instrumental mass bias, although all other possible correction schemes are monitored to assess data integrity. Using this approach, single Ni isotope analyses have uncertainties (2 se) on mass-bias-corrected  $\epsilon^{60}\text{Ni}$  and  $\epsilon^{62}\text{Ni}$  that are typically  $\leq \pm 0.13$  and  $\leq \pm 0.25$ , respectively (Fig. 1). Multiple analysis of samples results in uncertainties that are  $< \pm 0.05$  and  $< \pm 0.10$ , respectively (Fig. 1). Uncertainties (2 se) on <sup>62</sup>Ni/<sup>58</sup>Ni mass-bias-corrected  $\epsilon^{60}\text{Ni}$  and  $\epsilon^{61}\text{Ni}$  are also  $\leq \pm 0.05$  and  $\leq \pm 0.10$ , respectively. Some analyses were also carried out in pseudo-high resolution mode at a resolution of ca. 4000, which permits complete resolution of all interferences with the exception of Ni and Fe hydrides.

**Fig. 1.**  $\epsilon^{60}\text{Ni}$  and  $\epsilon^{62}\text{Ni}$  values of repeated Ni isotopic measurements ( $n = 9$ ) of the IIICD iron Mundrabilla.



**Preliminary Results:** The meteorites studied here include Fe-Ni metal from two iron meteorites and two main group pallasites (PMG) (Table 1). The irons include examples that Hf-W isotopic systematics [5] suggest formed very early in the Solar System.

Selected Ni isotopic data are reported in Table 1. Nickel isotopes exhibit very limited variations compared to the terrestrial standard.  $\epsilon^{60}\text{Ni}$  values range from +0.016 to -0.089 with Arispe having the most negative value that, given analytical uncertainties, is barely statistically resolvable from the analysis of Mundrabilla (+0.016).  $\epsilon^{62}\text{Ni}$  values range from +0.107 to -0.042, although  $\epsilon^{62}\text{Ni}$  values for all four irons and pallasites are identical within analytical uncertainty and yield a weighted average of all four samples of  $\epsilon^{62}\text{Ni} = +0.060 \pm 0.073$ . However, the two irons may have  $\epsilon^{62}\text{Ni}$  values that are marginally higher (0.010  $\epsilon$  units) than the terrestrial standard.

Three separate digestions of metal from the pallasite Esquel including a sample prepared in Copenhagen whose results were published in [3] all produced statistically identical results. Several analyses of one of these digestions for Esquel were made in pseudo-high resolution mode with the results showing no significant

difference from analyses made in low-resolution mode (Table 1).

**Table 1** Preliminary Ni isotope data for irons and pallasites (# = measured at a mass resolution > 4000).

Sample	Type	$\delta^{61}\text{Ni}$ ( $\pm 2$ se)	$\epsilon^{60}\text{Ni}$ ( $\pm 2$ se)	$\epsilon^{62}\text{Ni}$ ( $\pm 2$ se)	n
Arispe	IC iron	-0.96 (0.07)	-0.089 (0.024)	+0.073 (0.035)	9
Mundrabilla	IIICD iron	+0.14 (0.03)	+0.016 (0.042)	+0.107 (0.077)	9
Brenham	PMG	-0.10 (0.18)	-0.021 (0.046)	-0.042 (0.128)	10
Esquel	PMG	0.21 (0.05)	-0.040 (0.037)	-0.005 (0.072)	24
Esquel#	PMG	0.09 (0.07)	+0.030 (0.044)	+0.046 (0.109)	6

**Discussion:** The preliminary results of this study differ from those for irons and pallasites recently published by [3], which reported a mean deficit for  $\epsilon^{60}\text{Ni} = -0.024$  and large negative  $\epsilon^{62}\text{Ni}$  values up to -0.069 for irons and pallasites. Irrespective of which dataset is inaccurate or, indeed, whether both are inaccurate, it is clear given the levels of precision now obtainable that isobaric interferences during MC-ICPMS analysis can compromise the acquisition of accurate Ni isotope data and interpretations based on such data.

Taken at face value, the data produced in this study do not clearly reveal significant deficits in  $^{60}\text{Ni}$  that might be attributed to a late (or early) supernova  $^{60}\text{Fe}$  input into the young Solar System, or large  $^{62}\text{Ni}$  variations in irons and pallasites that are significantly different from Earth that might represent preservation of Ni nucleosynthetic variability in these samples on a planetary scale in the Solar System. However, further work is necessary to assess if the accuracy of our data is comparable to the analytical precision, before such a simplistic interpretation can be considered.

#### References:

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