



## Determination of Ni isotopes in nickel material from the Rossi reactor

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### 1) Task

Analyses of the Ni isotopic composition in material from the Rossi reactor experiments in order to determine if the material used in the reactor have an isotopic composition different from natural Ni present on Earth.

### 2) Material

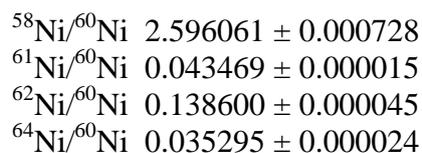
Two samples: one with dissolved Ni powder, “new” and one sample that with Ni powder used in the reactor, “used” was obtained from Sven Kullander. The powder samples had previously been dissolved and analyzed for elemental composition using ICP-MS. According to the report by Sven Kullander (June, 2011) the powders (150 mg) were dissolved in hydrochloric and nitric acids with some residues, probably carbides. Table 1 show the result from the ICP-MS analysis in Uppsala and demonstrate that the “new” sample is basically pure Ni, whereas the “used” sample also contain substantial amount of Cu, Fe, and Zn.

	<b>Copper</b>	<b>Nickel</b>	<b>Iron</b>	<b>Zinc</b>	<b>Lithium</b>
<b>Unused nickel</b>	0	103	0	0.6	0
<b>Used nickel</b>	9.6	62	11	0.4	0.4

Table 1. Percentages of different elements as measured using the ICP method in Uppsala

### 3) Stable Ni isotopes and standards

In August 2011 we purchased SRM (Standard Reference Material) 986 which is an isotopic standard for Ni. Natural Ni has 5 stable isotopes with abundances reported in Table 2. The atomic weight is  $58.6934 \pm 0.0002$  and the absolute isotopic ratios are:



The *SRM986* and a second standard with natural Ni the *Alfa Aesar ICP Ni standard* were used as our two standards to set up measurement routines and as for fractionation correction and normalization of the data. The *Alfa Aesar standard* was also used to estimate the reproducibility of our isotope measurements.

#### 4) Isotopic measurements using MC-ICP-MS

All the isotope measurements were carried out in the Laboratory of Isotope Geology at the Swedish Museum of Natural History using an *IsoProbe*, which is a Multiple Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS). The *IsoProbe* is equipped with 9 Faraday detectors for simultaneous determination of 9 masses (ion beams). For details regarding the instrument and determination of the isotopic composition of stable metal isotopes see, Fehr *et al.* (2008). Due to the large range in abundance with  $^{64}\text{Ni}$  being <1% of total Ni and because the Faraday cup detector can take a maximum signal of 10 V the nickel isotope analyses is challenging. The small isotope  $^{64}\text{Ni}$  is hampered by isobaric interferences from Zn and  $^{58}\text{Ni}$  from Fe, see Cook *et al.* (2006), which must be corrected for.

In order to determine the Ni isotopic composition of the “new” and “used” solutions using MC-ICP-MS several analytical issues must be solved which include: *mass bias* (mass fractionation) which can influence the measured isotope ratio up to several percent and is generated in the ICP source and mass spectrometer interface. *Isobaric interferences* from Zn, Fe and ArO (produced in the Ar ICP). *Matrix effects* derived from variable solution matrixes such as Cu and other elements and varying acids strength. *Blank contribution* from reagents, chromatography resin, laboratory equipment and nebulizer must be corrected for. Below follow a short description on our approach:

*Mass bias*: we decided to use the standard-sample–standard bracketing method. This means that unknown samples are analyzed between standards and basically each sample requires at least two standard runs. The measured ratios  $^x\text{Ni}/^{58}\text{Ni}$  are corrected for mass fractionation using an exponential law and the absolute Ni isotope ratios from *SRM986* following the description in Albarède & Beard (2004). For each isotope we compare the obtained ratio with that of the standard following the equation 1:

$$(R_i)_{\text{sample}} = (R_i)_{\text{std}} * (r_i)_{\text{sample}} / \sqrt{(r_i)_{\text{std}}^{\text{brack1}} * (r_i)_{\text{std}}^{\text{brack2}}} \quad (\text{eq. 1})$$

where  $R_i$  is the  $^x\text{Ni}/^{58}\text{Ni}$  ratios and  $x = ^{60}\text{Ni}, ^{61}\text{Ni}, ^{62}\text{Ni}, ^{64}\text{Ni}$ . ”brack1” and ”brack2” is NIST standard analyzed before and after the unknown.

$$\varepsilon_i = (R_i^{\text{sample}} / R_i^{\text{NIST}} - 1) * 10000 \quad (\text{eq. 2})$$

By this method (eq. 2) we basically determine the difference between the samples and the *SRM986* standard reported in parts per 10 000 (0.01%). This is however, not strictly followed as the  $^{64}\text{Ni}$  must be normalized to  $^{62}\text{Ni}$  in order to carry out the Zn isobar correction. The samples were analyzed in the following sequence *blank-SRM986-sample-blank-SRM986*, where sample is “new”, “used” and *Alfa Aesar*. There are other methods to address the mass bias but this is commonly used for MC-ICP-MS and stable metal isotopes.

*Isobaric interferences*: The used sample contain isobars from Fe and Zn that must be removed as complete as possible from the sample. Nickel was separated from the matrix using a

combination of anion and cation exchange chromatography columns by modifying the procedures in Chen et al. (2009). In total four columns were used to obtain a “clean” sample. It is also important to monitor the yield of the column separation as it has been demonstrated that isotopic fractionation, up to several per mil, can occur on chromatographic columns if the yield is too low. The isobaric interferences from ArO were partly removed by introduction of N<sub>2</sub> in the nebulizer system during analyses.

*Matrix effects.* In order to reduce the influence of varying matrix composition on the isotope determination all samples were evaporated to dryness after separation and re-dissolved in similar acid concentration. The Ni concentrations in samples and standards were matched to  $\pm 50$  mV at 8-9 V intensity of the largest peak.

*Blank contribution.* The blanks from reagents and equipment were determined only semi-quantitative. However, the Ni concentrations of the samples are sufficiently strong so that the blank contribution is probably not a major issue.

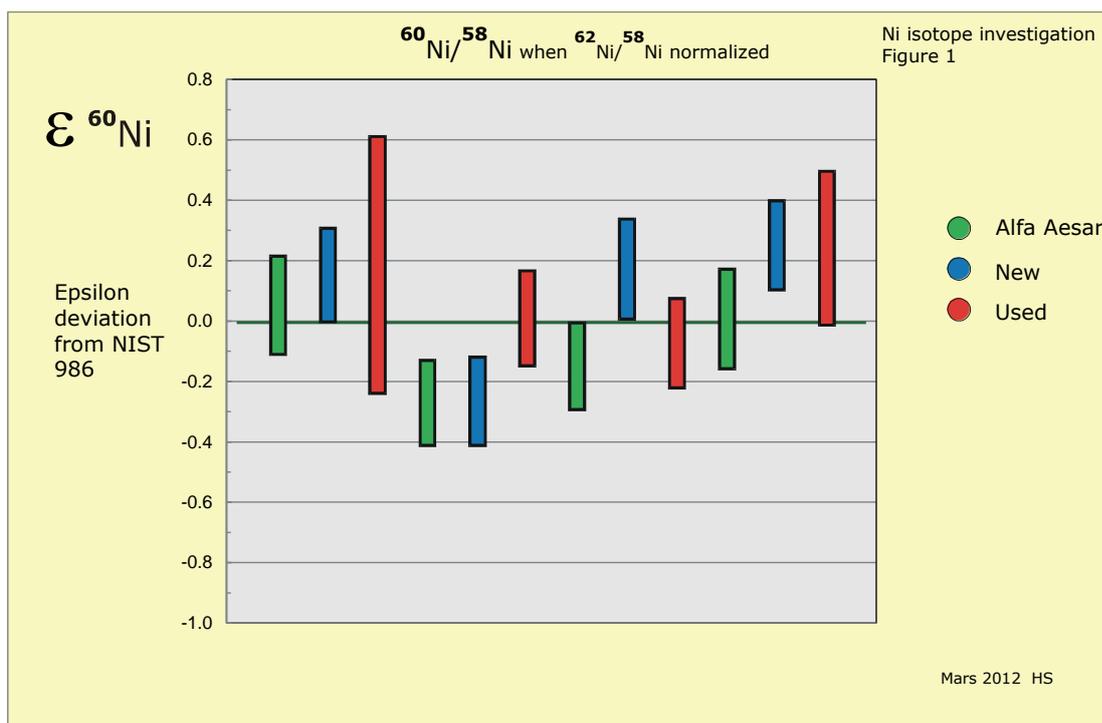
After chemical separation and matrix adjustment all 5 Ni isotopes were determined simultaneously using two different cup configurations. Using two configurations is necessary in order to make a correction from Fe and Zn isobars on Ni. For each sample also the isobaric interferences were monitored (58 interference monitored on <sup>57</sup>Fe, 64 interference monitored on <sup>66</sup>Zn) and the remaining interference (most removed by N<sub>2</sub> collision) from Ar<sup>18</sup>O <20mV and ArNe <5mV were compensated by on peak blank reduction.

## 5) Results

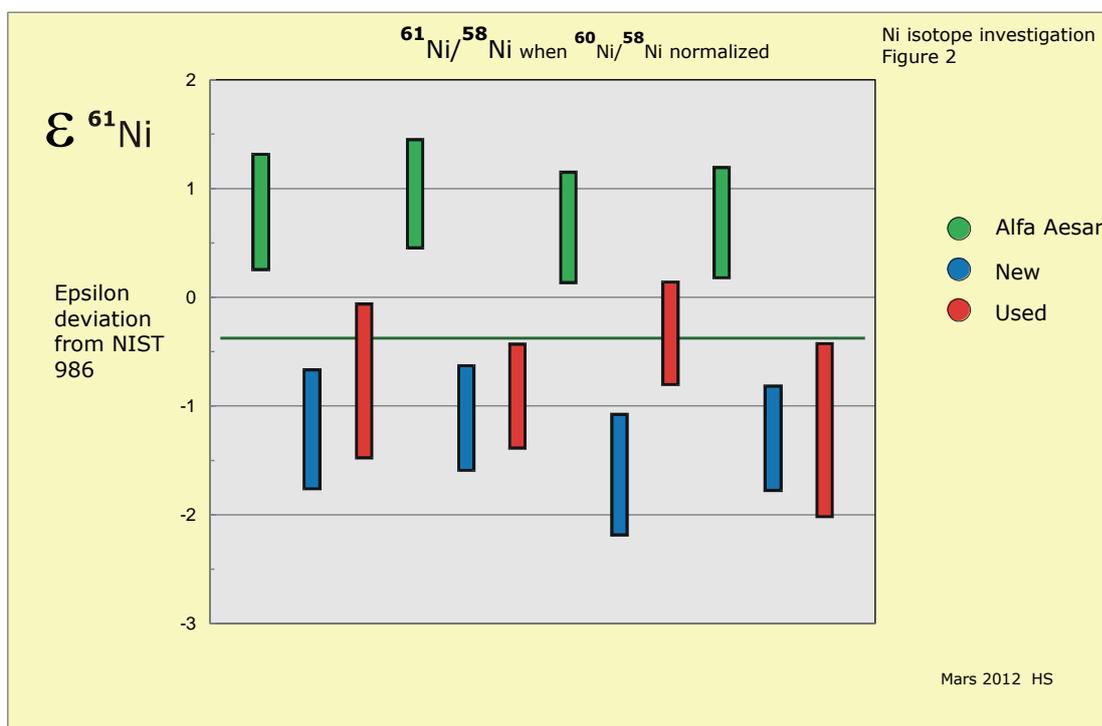
The results for  $\epsilon^{60}\text{Ni}$  (<sup>60</sup>Ni/<sup>58</sup>Ni),  $\epsilon^{61}\text{Ni}$  (<sup>61</sup>Ni/<sup>58</sup>Ni),  $\epsilon^{62}\text{Ni}$  (<sup>62</sup>Ni/<sup>58</sup>Ni),  $\epsilon^{64}\text{Ni}$  (<sup>64</sup>Ni/<sup>62</sup>Ni) for the *Alfa Aesar* standard (green bar) and for the new (blue bar) and used (red bar) Ni powders are reported in **Figure 1 to 4**.

All Figures have a similar outline with deviations in the isotope ratio <sup>x</sup>Ni/<sup>58</sup>N (<sup>64</sup>Ni/<sup>62</sup>Ni) in  $\epsilon$ -units (parts per 10 000) from that of the *SRM986* standard reported on the vertical axis and sample run on the horizontal axis. An  $\epsilon = 0$  mean that the isotope ratio is similar to that of the *SRM986* standard. The height of the bars is the reported error for each analysis.

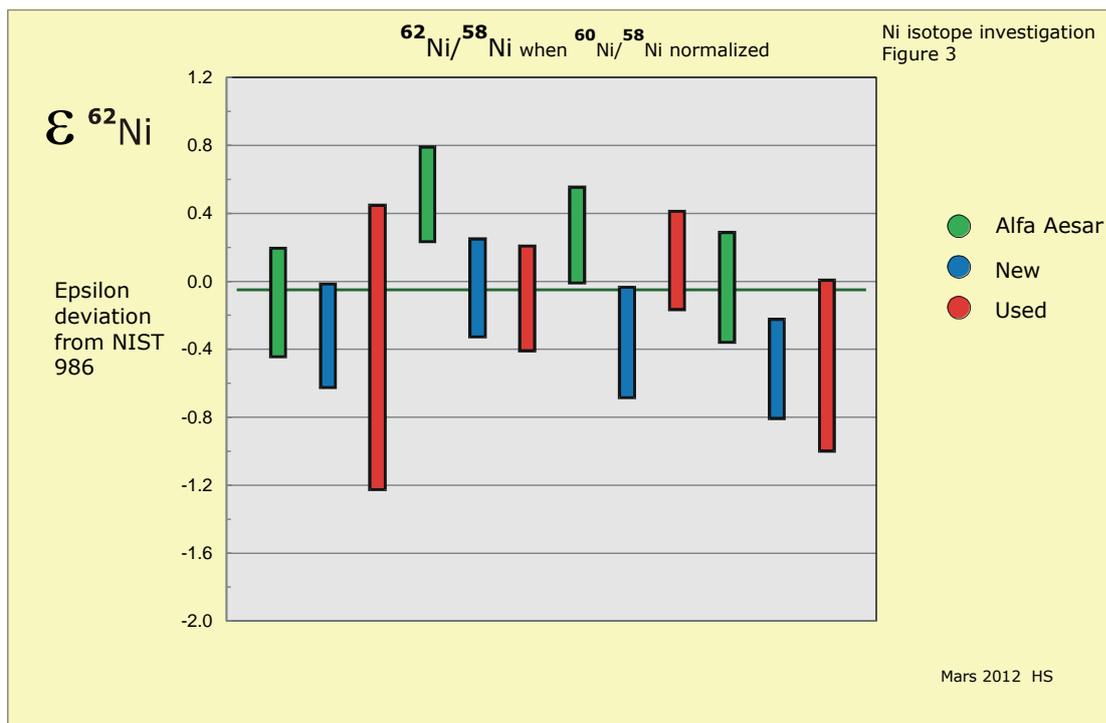
For each sample the analytical sequence *blank-SRM986-sample-blank-SRM986* was carried out. This has been repeated four times for each sample so that each figure report four different runs for both samples and *Alfa Aesar* standard.



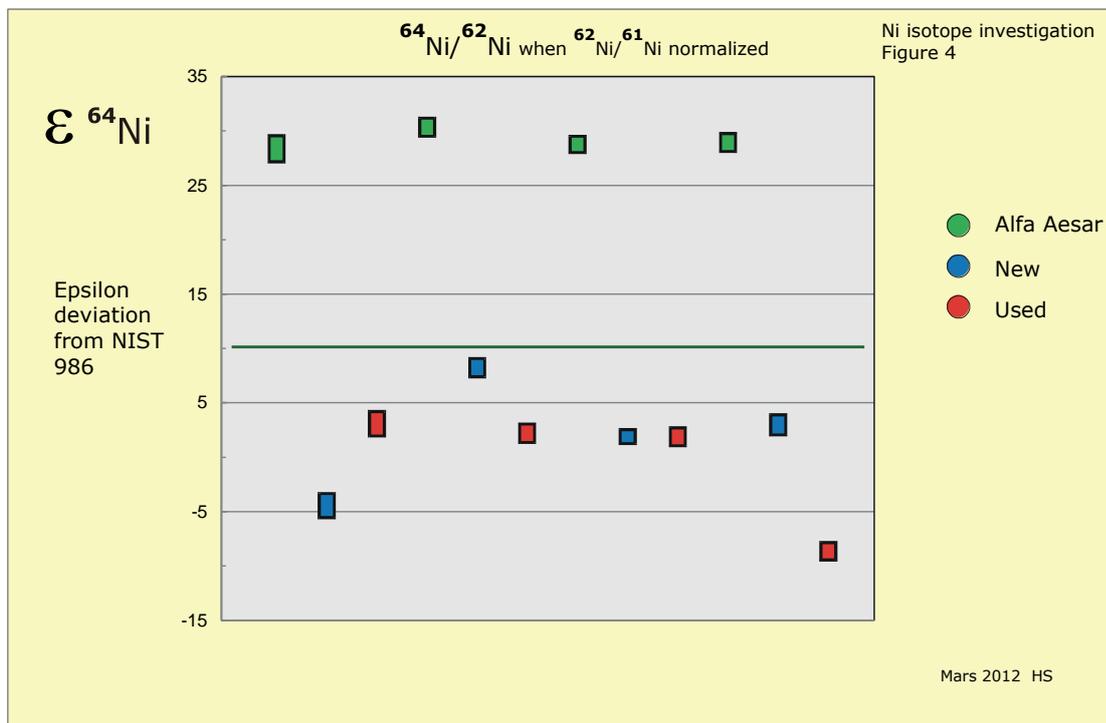
**Figure 1.** The  $\epsilon^{60}\text{Ni}$  ( $^{60}\text{Ni}/^{58}\text{Ni}$ ) using the  $^{62}\text{Ni}/^{58}\text{Ni}$  ratio for normalization for the mass bias correction. The reproducibility is estimated to  $\pm 0.3\epsilon\text{u}$  from the *Alfa Aesar* standard. There is no significant difference for the  $\epsilon^{60}\text{Ni}$  between the new and used sample compared to the *SRM986* standard.



**Figure 2.** The  $\epsilon^{61}\text{Ni}$  ( $^{61}\text{Ni}/^{58}\text{Ni}$ ) using the  $^{60}\text{Ni}/^{58}\text{Ni}$  ratio for normalization for the mass bias correction. The reproducibility is estimated to  $\pm 0.3\epsilon\text{u}$  from the *Alfa Aesar* standard. The *Alfa Aesar* standard deviates from that of the new and used samples and this is most likely related to matrix effects, because this solution has a slightly different matrix compared to the samples prepared in our laboratory. There is no significant difference for the  $\epsilon^{61}\text{Ni}$  between the new and used samples and compared to the *SRM986* standard.



**Figure 3.** The  $\epsilon^{62}\text{Ni}$  ( $^{62}\text{Ni}/^{58}\text{Ni}$ ) using the  $^{60}\text{Ni}/^{58}\text{Ni}$  ratio for normalization for the mass bias correction. The reproducibility is estimated to  $\pm 0.6 \epsilon\text{u}$  from the *Alfa Aesar* standard. There is no significant difference for the  $\epsilon^{60}\text{Ni}$  between the new and used sample compared to the *SRM986* standard.



**Figure 4.** The  $\epsilon^{64}\text{Ni}$  ( $^{64}\text{Ni}/^{62}\text{Ni}$ ) using the  $^{62}\text{Ni}/^{61}\text{Ni}$  ratio for normalization for the mass bias correction. The reproducibility is estimated to  $\pm 2 \epsilon\text{u}$  from the *Alfa Aesar* standard. The deviations for the *Alfa Aesar* from the *SRM986* is large, about  $30\epsilon\text{u}$  and this is probably related to a combination of matrix effects and the way we have chosen to carry out the isobaric interference corrections. It is important to acknowledge that the  $^{64}\text{Ni}$  isotope only constitute only 0.9% of natural Ni and is thus very hard to determine precisely (*i.e.* if the  $^{58}\text{Ni}$  is signal is 8V the  $^{64}\text{Ni}$  is only about 7 mV). There is no significant difference for the  $\epsilon^{60}\text{Ni}$  between the new and used sample compared to the *SRM986* standard.

From the measured isotope ratios we calculate the abundance for each stable Ni isotope in the “new” and “used” samples and the results are reported along with the data for the NIST Ni standard in Table 2. The errors in the abundances are determined from the short term reproducibility (n=4) during this measurement session. There is no significant difference in the abundance of the stable Ni isotopes between “new” and “used” samples and the NIST standard. Clearly all Ni we have analyzed show an isotopic composition similar to natural terrestrial Ni.

	new			used			NIST <sub>std</sub>		
	%		2σ	%		2σ	%		2σ
<sup>58</sup> Ni	68.0768	±	0.0024	68.0770	±	0.0047	68.0769	±	0.0059
<sup>60</sup> Ni	26.2233	±	0.0047	26.2232	±	0.0034	26.2231	±	0.0051
<sup>61</sup> Ni	1.1397	±	0.0018	1.1398	±	0.0017	1.13989	±	0.00043
<sup>62</sup> Ni	3.6344	±	0.0049	3.6345	±	0.0063	3.6345	±	0.0011
<sup>64</sup> Ni	0.926	±	0.057	0.925	±	0.090	0.92555	±	0.00060

Table 2. Calculated abundances (at%) of the Ni isotopes in Ni powder “new” and “used” and also reported values for the NIST standard.

## 6) Conclusions

- We have developed a method to measure the stable Ni isotopic composition using, column chromatography separation and MC-ICP-MS. With this method and using the *Alfa Aesar* as a standard we estimate our reproducibility for Ni isotopes to be:  $\epsilon^{60}\text{Ni} \pm 0.3$ ,  $\epsilon^{61}\text{Ni} \pm 0.3$ ,  $\epsilon^{62}\text{Ni} \pm 0.6$ ,  $\epsilon^{64}\text{Ni} \pm 2$
- Given these uncertainties there are no significant difference in Ni isotope composition between the new and used material solutions given to us by Sven Kullander.
- There is no significant difference in the isotopic abundances between the new and used solutions and terrestrial nickel (*SRM986*).

## 7) References

- Albarède and Beard (2004) *Reviews in Mineralogy and Geochemistry* 55, 113-152.
- Chen J.H., Papanastassiou and Wasserburg G.J. (2009) *Geochim. Cosmochim. Acta* 73, 1461-1471.
- Cook D., Wadhwa M., Janney P.E., Dauphas N., Clayton R.N. and Davis A. (2006) *Anal. Chem.* 78, 8477-8484.
- Fehr M., Andersson P., Hålenius U. and Mörth C.-M. (2008) *Geochim. Cosmochim. Acta* 72, 807-826.