

**DEVELOPMENT OF MULTI-COLLECTION Ni ISOTOPIC ANALYSIS OF FERROMAGNESIAN SILICATES IN THE ION MICROPROBE.** G. R. Huss<sup>1</sup>, S. Tachibana<sup>2</sup>, K. Nagashima<sup>1</sup>, and M. Telus<sup>1</sup>, <sup>1</sup>HIGP/SOEST, University of Hawai'i at Mānoa, 1680 East-West Road, Honolulu, HI 96822 ([ghuss@higp.hawaii.edu](mailto:ghuss@higp.hawaii.edu)), <sup>2</sup>Department of Earth and Planetary Science, University of Tokyo, 7-3-1 Hongo, Tokyo 113-0033, Japan.

**Introduction:** Iron-60 decays to <sup>60</sup>Ni with a half-life of  $\sim 2.6 \times 10^6$  yr [1]. Its presence in the early solar system has been demonstrated by measurements of chondrites [2-6] and differentiated meteorites [7-9]. Its short half-life makes it both a potential early solar system chronometer and a heat source for asteroidal differentiation and metamorphism. Because <sup>60</sup>Fe is produced only in stars, it also provides an important constraint on the environment where the solar system formed [10]. The ion microprobe has been an important tool for studying the <sup>60</sup>Fe-<sup>60</sup>Ni system, but analyses are not yet routine. Last year [6], we reported on our initial attempts to use multi-collection on the Cameca ims 1280 ion microprobe at the University of Hawai'i to measure the <sup>60</sup>Fe-<sup>60</sup>Ni system. This year we report on a modified method that solves several of the most difficult analytical problems. We also present preliminary results on a radiating pyroxene chondrule from Semarkona (LL3.0).

**Experimental Technique:** We measure iron and nickel isotopes as positive ions using an <sup>16</sup>O<sup>+</sup> primary beam. A mass resolving power (MRP) of  $\sim 4200$  (10% valley definition) was achieved using slit #2 of the multi-collector (250 microns) and a 77 micron entrance slit. The multi-collector was set up to measure <sup>60</sup>Ni, <sup>61</sup>Ni, and <sup>62</sup>Ni simultaneously on electron multipliers, with a field jump used to measure either <sup>56</sup>Fe or <sup>57</sup>Fe on a multicollector Faraday cup. By placing the detector for <sup>61</sup>Ni as close to the optical axis of the mass spectrometer as possible, we minimize the defocusing of the off-axis beams and improved the peak shape. By jumping to <sup>56</sup>Fe or <sup>57</sup>Fe for three seconds every sixty seconds, we give the multipliers a brief rest, which appears to improve multiplier stability. We use this technique when measuring oxygen isotopes to minimize multiplier aging [11]. As an additional precaution against multiplier aging, we limited the <sup>60</sup>Ni count rate to a few thousand counts per second by limiting the primary beam current to  $\sim 1$  nA. After setting the gain of the multipliers, we did not expose them to high count rates for the duration of the measurements. This measurement protocol eliminated the detector instability that plagued our earlier attempts to measure with the multi-collector.

A MRP of  $\sim 4200$  is insufficient to resolve the <sup>60</sup>NiH interference on <sup>61</sup>Ni. We measure the <sup>61</sup>Ni/<sup>62</sup>Ni ratio to monitor the instrumental mass fractionation and any intrinsic mass fractionation in the sample. To minimize the contribution of the hydride, we main-

tained the sample chamber pressure in the mid  $10^{-10}$  torr range. Measurements at higher MRP using the monocollector showed the contribution of the hydride to be  $\leq 1$  % on both standard and sample.

The new protocol produced very consistent results on the hypersthene standard. Reproducibility with a single setup was  $\pm 2\%$  ( $2\sigma$ ) for <sup>60</sup>Ni/<sup>62</sup>Ni and <sup>61</sup>Ni/<sup>62</sup>Ni. For Semarkona data with low Fe/Ni ratios, the <sup>61</sup>Ni/<sup>62</sup>Ni ratio was unresolved from the standard values, giving us confidence in the validity of using an external fractionation correction. The external fractionation correction and the improved counting statistics relative to mono-collection will permit determination of (<sup>60</sup>Fe/<sup>56</sup>Fe)<sub>0</sub> with a precision 2-5 times better than we reported previously [4,5] for similar samples.

However, the improved precision and reproducibility revealed a problem that we had not appreciated previously. Each nickel isotope has molecular interferences that are nominally resolved by a MRP of  $\sim 4200$  [<sup>30</sup>Si<sub>2</sub> and <sup>44</sup>Ca<sup>16</sup>O for <sup>60</sup>Ni (required MRP 3578, 3051); <sup>45</sup>Sc<sup>16</sup>O for <sup>61</sup>Ni (3087); <sup>46</sup>Ca<sup>16</sup>O and <sup>46</sup>Ti<sup>16</sup>O for <sup>62</sup>Ni (3225, 3066)]. However, the interference peaks are 5 to 10 times larger than the nickel peaks on our hypersthene standard (even larger relative to nickel in the sample), and the abundance sensitivity of the 1280 is insufficient to completely eliminate the tails of the interferences at the nickel peaks. In addition, the multi-collector works best with a small primary beam spot and low degree of charging. As the effective hole diameter increases, the peak shapes degrade and the interferences have increasing significance, especially when the Fe/Ni ratio is very high. The same problem may have been present last year [6], but because detector problems and tuning issues were so severe, we did not recognize it. The data that we believe are most reliable for the sample reported here are those with <sup>56</sup>Fe/<sup>62</sup>Ni ratios  $< \sim 600,000$ . For spots with higher <sup>56</sup>Fe/<sup>62</sup>Ni ratios, interferences were unmanageable. Below we discuss methods to deal with this problem.

**Results:** The new protocol potentially gives a significant improvement in precision compared to our previous work [4-6]. Figure 1 shows new preliminary data for Semarkona radiating-pyroxene chondrule D1. The <sup>60</sup>Ni/<sup>62</sup>Ni ratios correlates positively with Fe/Ni ratio, but because of the interference problem discussed above, we cannot extract a firm number for (<sup>60</sup>Fe/<sup>56</sup>Fe)<sub>0</sub> from these data. A regression through all of the data gives a slope of  $(0.80 \pm 0.38) \times 10^{-7}$  with a high intercept. Forcing the regression through normal

$^{60}\text{Ni}/^{62}\text{Ni}$  gives a steep slope. A regression through the points with  $^{56}\text{Fe}/^{62}\text{Ni} < 600,000$ , gives  $(^{60}\text{Fe}/^{56}\text{Fe})_0 = (2.3 \pm 1.2) \times 10^{-7}$ . Forced through normal  $^{60}\text{Ni}/^{62}\text{Ni}$ , the regression gives  $(^{60}\text{Fe}/^{56}\text{Fe})_0 = (3.4 \pm 0.7) \times 10^{-7}$ . Although the initial ratio for this chondrule is still quite uncertain, the results are broadly consistent with previous results [4-6]. We expect to provide final data for this chondrule at the conference.

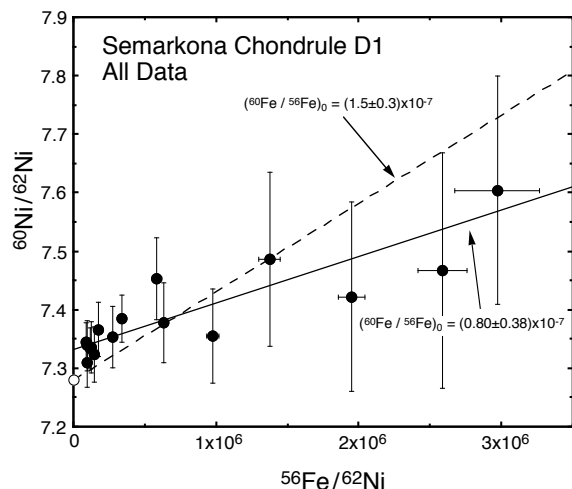


Fig. 1: All data for Semarkona D1. Solid line is regression of black data points. Dashed line is regression forced through normal Ni (open symbol).

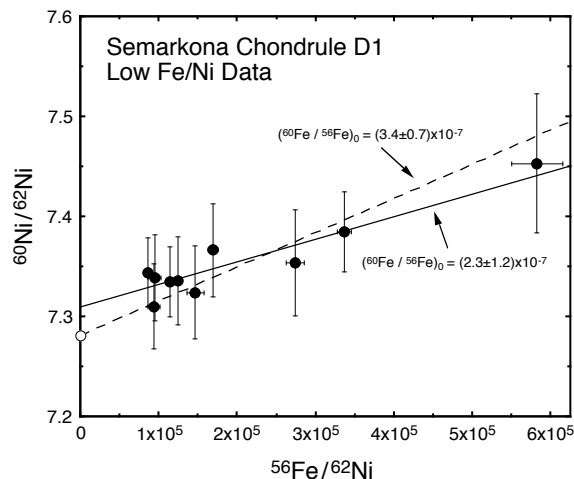


Fig. 2: Low-Fe/Ni data for Semarkona D1. Symbols the same as in Fig. 1.

**Discussion:** We have been working to establish an experimental protocol that permits us to apply the full analytical power of the 1280 to the  $^{60}\text{Fe}$  problem. There are several potential ways to reduce or eliminate the interferences. One way is to increase the MRP of the instrument. When we were using the mono-collector, we did not see contributions from the molecular interferences listed above. There are two reasons for this: 1) The mono-collector electron multi-

plier is positioned on the optical axis of the mass spectrometer, with the result that the image of the entrance slit can be focused exactly on the exit-slit plane. 2) We operated the mono-collector at a MRP of  $\sim 5000$ , significantly higher than is currently possible with the multi-collector. A potential solution to this problem is to reconfigure the exit slits on the multi-collector. The 1280 currently has three exit slit positions with slit widths of 500, 250, and 150 microns. The 150-micron slit has not been useful for isotopic analysis. A slit of  $\sim 200$  microns in position #3 would give us higher MRP, between 5000 and 6000 depending on details of the tuning, and should still be wide enough to permit stable tuning for measurements.

A second way to deal with the interferences is to reduce their count rates relative to those of the nickel isotopes. This can be achieved by energy filtering [e.g., 12]. Work with other isotope systems suggests that 30-40 eV of energy filtering can significantly suppress the molecular ions while leaving good count rates for atomic ions. We will investigate this possibility over the next few weeks.

We tested using the  $\text{Cs}^+$  ion source and measuring the nickel isotopes as negative ions as a way to reduce the interferences. This has been shown to work for metal and sulfide [13], but it does not work on silicates. First, the hydride is significantly larger,  $\sim 2\text{-}3\%$  of the  $^{61}\text{Ni}$  signal. Second, although the relative abundances of potential molecular interferences are different than with the  $\text{O}^-$  source,  $\text{SiO}_2$  is present at all three masses at abundances  $10^3\text{-}10^4$  times higher than the nickel peaks. Although the nominal MRP to exclude these peaks is low ( $\sim 1800$ ), the poor abundance sensitivity and the very high abundances of these molecules make the interferences very large. For example, the tail of the  $^{28}\text{Si}^{16}\text{O}_2$  peak contributes  $\sim 2\text{-}3\%$  to the signal at  $^{60}\text{Ni}$  on our hypersthene standard.

**References:** [1] Rugel G. et al. (2009) *Phys. Rev. Lett.* 103, 072502. [2] Tachibana S. and Huss G. R. (2003) *Ap. J.* 588, L41-L44. [3] Mostefaoui S. et al. (2005) *Ap. J.* 625, 271-277. [4] Tachibana S. et al. (2006) *Ap. J.* 639, L87-L90. [5] Tachibana S. et al. (2007) *LPS XXXVIII*, #1709. [6] Tachibana et al. (2009) *LPS XL*, #1808. [7] Shuykolyukov A. and Lugmair G. W. (1993) *Science* 259, 1138-1142. [8] Bizzarro M. et al. (2007) *Science* 316, 1178-1181. [9] Quitté G. et al. (2009) *LPS XXXVI*, #1827. [10] Takigawa A. et al. (2008) *Ap. J.* 688, 1382-1387. [11] Makide K. K. et al. (2009) *GCA* 73, 5018-5050. [12] Zinner E and Crozaz G. (1986) *Int. J. Mass Spec. Ion Proc.* 69, 17-38. [13] Mostefaoui and Bourot-Denise (2009) *MAPS* 44, A149. Supported by NASA, NNX08AG58G (GRH) and Grant-in-Aids for Scientific Research (20684025) (ST).