

HIGH PRECISION NICKEL ISOTOPIC ANALYSES IN METEORITES. J. H. Chen¹, D. A. Papanastassiou², G. J. Wasserburg³, ^{1,2}Science Division, ¹M/S 183-601, ²M/S 183-335, Jet Propulsion Laboratory, Caltech, 4800 Oak Grove Dr., Pasadena, CA 91109-8099, ³The Lunatic Asylum, GPS Div., 170-25, Caltech, Pasadena, CA 91125 (James.H.Chen@jpl.nasa.gov).

Introduction. Evidence for ⁶⁰Fe ($\tau_{1/2} = 1.5$ Ma) has been obtained in eucrites [1-3], consisting of excesses in ⁶⁰Ni, in phases with high Fe/Ni, but no well-defined isochrons were determined. Tachibana and Huss [4] reported evidence for ⁶⁰Fe from measurements of ⁶⁰Ni excesses in troilite from Krymka and Bishunpur, with inferred initial ⁶⁰Fe/⁵⁶Fe of $(1.1 \pm 0.2) \times 10^{-7}$ and $(1.7 \pm 0.5) \times 10^{-7}$. Mostefaoui *et al.* [5] reported initial ⁶⁰Fe/⁵⁶Fe of $(7.3 \pm 2.6) \times 10^{-7}$ for FeS in Semarkona. These measurements were obtained with ion probes, in sulfide phases with very high Fe/Ni.

Recent work on Ni isotopes, using MC-ICP-MS, indicates a complex picture. Moynier *et al.* [6,7] showed excesses of up to 1.5 ϵ in ⁶⁰Ni/⁵⁸Ni in some chondrites and iron meteorites and reported an initial ⁶⁰Fe/⁵⁶Fe $(3 \pm 0.2) \times 10^{-6}$, higher than any previous estimate. Cook *et al.* [8] did not find any resolvable excess in ⁶⁰Ni/⁵⁸Ni at the level of ± 0.15 ϵ . Quitté *et al.* [9] analyzed FeNi and sulfide from iron meteorites and found no ⁶⁰Ni effects in the FeNi at $\pm 0.3\epsilon$. In some sulfides, they found large and correlated effects in $\epsilon^{60}\text{Ni}$ (-4.17 to +0.18 ϵ) and $\epsilon^{61}\text{Ni}$ (-0.81 to +17.23 ϵ). In irons, Bizzarro *et al.* [10], reported high precision Ni data and claimed small shifts of $-0.28 \pm 0.11\epsilon$ to $-0.11 \pm 0.07\epsilon$ in ⁶⁰Ni and $-0.61 \pm 0.27\epsilon$ to $-0.30 \pm 0.21\epsilon$ in ⁶²Ni. In Murchison, they reported normal ⁶⁰Ni/⁵⁸Ni, but a shift of 0.36 ± 0.10 ϵ in $\epsilon^{62}\text{Ni}$. Völkening and Papanastassiou [11, 12], using TIMS, determined Fe and Zn isotopic anomalies in FUN CAI. Birck and Lugmair [13] reported TIMS Ni results on Allende CAI and found shifts of a few ϵ in ⁶⁰Ni, ⁶²Ni and ⁶⁴Ni. If their Ni data are renormalized to ⁶²Ni/⁵⁸Ni, only 1 out of 5 inclusions shows a small $\epsilon^{60}\text{Ni} < 1\epsilon$.

Methods. We developed, last year, analytical techniques for the measurement of Ni isotopes by MC-ICP-MS and by TIMS [14]. In this work, we use TIMS, which shows fewer mass interference problems and, in our experience, yields more reliable results. We developed new chemical procedures for the separation of Ni, using several stages of ion exchange, solvent extraction, and precipitation, to minimize mass interferences from compounds of Ca, Mg, Sc, Ti, Fe, and Zn. We succeeded in removing most interfering impurities. In particular, interferences at mass 58 and 64 from ⁵⁸Fe and ⁶⁴Zn and from molecular ions were reduced to less than 1×10^{-6} and 2×10^{-4} , respectively. We also improved the thermal ionization efficiency for Ni to $\geq 1\%$. The Ni data are normalized to ⁶²Ni/⁵⁸Ni = 0.05338858 [15].

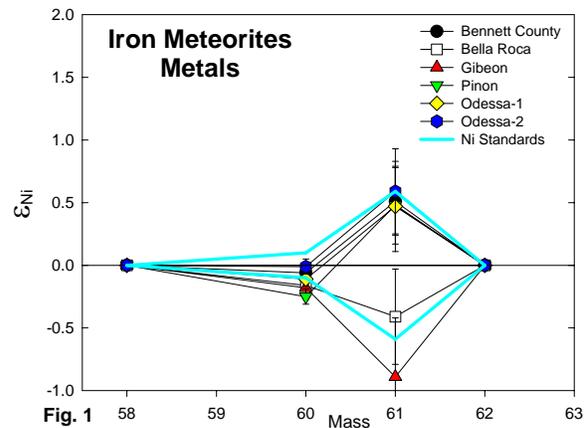


Fig. 1

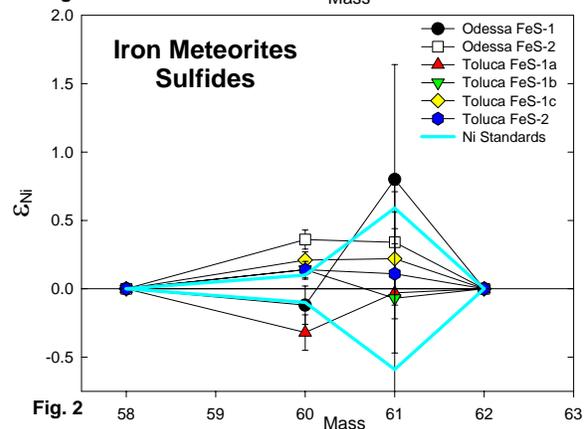


Fig. 2

Iron Meteorite Results. The reproducibilities for the Ni isotopes for a period of a few months are shown as an error envelope ($2\sigma_{\text{mean}}$, $n=14$) in Fig. 1-3, and are $\pm 0.1\epsilon$ for ⁶⁰Ni and $\pm 0.6\epsilon$ for ⁶¹Ni. Using TIMS, we determined that, for samples of FeNi from 5 iron meteorites of different groups (Bennett County, Bella Roca, Gibeon, Piñon and Odessa), the $\epsilon^{60}\text{Ni}$ are the same as terrestrial normal to within $\pm 0.1\epsilon$, and $\epsilon^{61}\text{Ni}$ are normal to $\pm 0.7\epsilon$ (Fig. 1). For ⁵⁶Fe/⁵⁸Ni in FeNi as low as 7 (Hoba, Piñon; i. e., enriched in Ni, relative to solar) and the limit ⁶⁰Fe/⁵⁶Fe $< 2.4 \times 10^{-7}$ (cf results on Chainpur, below) we expect a deficit in ⁶⁰Ni of -0.1ϵ , which is not resolvable. The Ni data on sulfide samples from two irons are shown in Fig. 2 and have larger uncertainties, due to low Ni concentrations and possibly some mass interference problems. Three analyses of a sulfide from Toluca (FeS-1a-c) and an analysis of a 2nd sulfide from Toluca (FeS-2) show normal values within the uncertainties. The data show no evidence for ⁶⁰Ni excesses and yield limits on ⁶⁰Fe/⁵⁶Fe of $< 2 \times 10^{-9}$ (measured ⁵⁶Fe/⁵⁸Ni=5200). Two sulfide samples (FeS-1 & FeS-2) from Odessa show larger uncertainties and

hints of up to $+0.4\epsilon$ shifts in ^{60}Ni and $+0.8\epsilon$ in ^{61}Ni . These two sulfide analyses showed unusual, higher interferences at mass 59 and these small shifts in Odessa sulfides could be due to residual mass interferences.

Chondrite Results: We have analyzed also two pyroxene chondrules from the Chainpur chondrite. The results indicate normal ^{60}Ni abundance to $\pm 0.5\epsilon$. For $^{56}\text{Fe}/^{58}\text{Ni}=48$ and 74 , for chondrules 1 and 2, we calculate initial values $^{60}\text{Fe}/^{56}\text{Fe} < 9 \times 10^{-8}$ and $< 2.4 \times 10^{-7}$. In addition, we analyzed the bulk meteorite and a sulfide from St. S everin (LL6). The specimen contains an unusually large sulfide vein (2mm \times 10mm) with a mixture of euhedral troilite crystals, massive sulfide and metal grains, indicating a primary origin of the sulfide. Analyses of the whole rock sample and three aliquots of the Ni from this sulfide vein are shown in Fig. 3. Analyses of the bulk and two analyses of the troilite show normal isotopic values. One analysis of the troilite sample shows a $+1.0\epsilon$ shift in ^{61}Ni and no resolvable effect in ^{60}Ni . With the measured $^{56}\text{Fe}/^{58}\text{Ni}$ of 1040, we calculate an initial $^{60}\text{Fe}/^{56}\text{Fe} < 4 \times 10^{-9}$.

Discussion. The Ni results we have obtained are in agreement with Ni isotope analyses on FeNi by [8,9,10]. However, we do not confirm the reported large isotopic shifts in the sulfides of either Toluca or Odessa using the MC-ICP-MS [9], indicating, from our experience, the greater potential danger of significant, hard to correct mass interferences for plasma ionization. We do not confirm any resolvable shifts for ^{60}Ni in FeNi in iron meteorites as reported by others using the MC-ICP-MS [6, 7]. The Chainpur chondrules show small Fe/Ni enrichment factors of ~ 3 relative to the average solar value. Therefore, we do not expect to find large shifts in ^{60}Ni . While St. S everin was formed early in the solar system with a U-Pb age of 4.552 AE [16], Re-Os data on the St. S everin sulfide [17] indicate a recent redistribution ($< 2.3\text{Ga}$), and it is, therefore, unlikely that effects in Ni would have been preserved in the sulfide.

Timmes *et al.* [18] reviewed the production of ^{26}Al and ^{60}Fe in Type II supernovae (SN) and pointed out the strong coproduction of these radionuclides in the O/Ne zone in massive stars. Using these calculations, Wasserburg *et al.* [19] obtained an average production ratio for $^{26}\text{Al}/^{60}\text{Fe} \sim 8.6$ for contributions to the solar nebula, from SNIIs. Based on the typical $(^{26}\text{Al}/^{27}\text{Al})_0$ in CAI, they calculated for a SNIi source, $^{60}\text{Fe}/^{56}\text{Fe}$ between 3×10^{-7} and 1×10^{-5} . They viewed a search for ^{60}Ni effects as a sensitive test for a supernova trigger for the formation of the solar system. For the solar $^{60}\text{Ni}/^{56}\text{Fe} = 0.0156$ ($^{56}\text{Fe}/^{58}\text{Ni}=25$), shifts in ^{60}Ni of 0.2 to 8.3ϵ would be expected. Therefore, enrichments in Fe/Ni in mineral phases of only a factor of 10 above the solar value should yield clear effects in CAI and also in ordinary chondrules, if they formed in the first three

million years, of solar system history. ^{60}Ni effects in

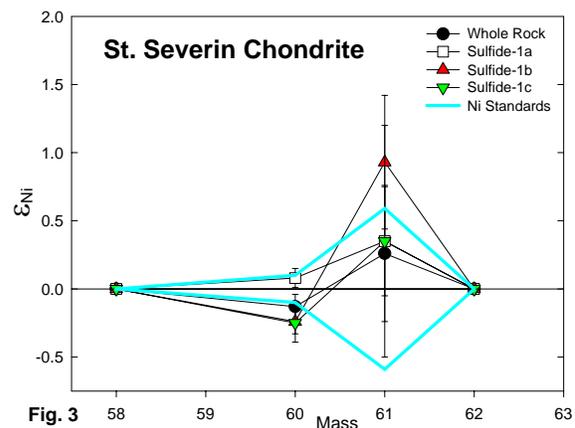


Fig. 3

CAI and in ordinary chondrules would be important as a test of whether the observed ^{26}Al in CAI can be associated with a SNIi provenance. The results on Chainpur chondrules indicate a limit of $^{60}\text{Fe}/^{56}\text{Fe} < 2.8 \times 10^{-7}$, which is compatible with initial ratio reported by [4]. There is clearly a need for a continued search for effects in high Fe/Ni chondrules, in unmetamorphosed chondrites.

References. [1] Shukolyukov A. & Lugmair G. W. (1993a) *EPSL* 119, 159. [2] *ditto* (1993b) *Science* 259, 1138. [3] Lugmair G. W., Shukolyukov A., & MacIsaac C. (1996) *LPS XXVII*, 785. [4] Tachibana S. & Huss G. R. (2003) *Ap. J. Letters* 588, L41. [5] Mostefaoui S., Lugmair G. W., Hoppe P., & El Goresy A. (2004) *New Astron. Rev.* 48, 155. [6] Moynier F., Telouk P., Blichert-Toft J. & Albar ede F. (2004) *LPS XXXV*, #1286. [7] Moynier F., Blichert-Toft J., Telouk P. & Albar ede F. (2005) *LPS XXXV*, #1286. [8] Cook D. L., Wadhwa M., Clayton R. N., Janney P. E., Dauphas N. & Davis A. M. (2005) *LPS XXXVI*, #1779. [9] Quitt e G., Meier M., Latkoczy C., Halliday A. N. & Gunther D. (2006) *EPSL* 242, 16. [10] Bizzarro M., Ulfbeck D. & Thrane K. (2006) *LPS XXXVII*, #2020. [11] V olkening J. & Papanastassiou D. A. (1989) *Ap. J. Lett.* 347, L43. [12] *ditto* (1990) *ibid.* 358, L29. [13] Birck J. L. & Lugmair G. W. (1988) *EPSL*, 90, 131. [14] Chen J. H. & Papanastassiou D. A. (2006) *LPS XXXVII*, #1997. [15] Gramlich J. W. *et al.* (1989) *J. Res. NIST.* 94, 347-356. [16] Chen J. H. & Wasserburg G. J. (1981) *EPSL* 52, 1. [17] Chen *et al.* (1998) *GCA* 62, 3379. [18] Timmes F. X., Woosley S. E., Hartmann D. H., Hoffman R. D. & Weaver T. (1995) *Ap. J.* 449, 204. [19] Wasserburg G. J., Gallino R. & Busso M. (1998) *Ap. J. Lett.* 500, L189.

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