

LOW-LEVEL MAGNESIUM ISOTOPIC ANALYSIS FOR THE GENESIS MISSION. M. Humayun¹ and S. Huang^{1,2}, ¹National High Magnetic Field Laboratory & Dept. of the Geological Sciences, Florida State University, 1800 E. Paul Dirac Drive, Tallahassee, FL 32310, USA (humayun@magnet.fsu.edu), ²Dept. of Earth & Planetary Sciences, Harvard University, Cambridge, MA 02189, USA (huang17@fas.harvard.edu).

Introduction: The Sun includes 99.9% of the mass of the solar system, so analysis of the isotopic compositions of elements from the Sun should be representative of the initial and/or bulk isotopic composition of planetary materials. Gravitational settling from the Outer Convection Zone (OCZ) of the Sun may contribute towards systematic light isotope enrichment of a few per mil detectable in the solar wind [1]. During the generation of the solar wind, isotopic fractionation of accelerated ions is expected due to inefficient coulomb drag [1, 2]. Enrichment of the lighter isotopes of noble gases has been reported in GENESIS DoS wafers [3], but not confirmed in AloS [4]. Magnesium isotopic composition is a major target for solar astrophysics because it is a low FIP (7.6 eV) element with three isotopes that have favorable abundances for precise determination (²⁴Mg: 78.99 %, ²⁵Mg: 10.00 %, ²⁶Mg: 11.01 %) and no atomic isobaric interferences [5, 6, 7]. The predicted mass fractionation in Mg is on the order of tens of per mil (dominantly from inefficient coulomb drag) [1], but spacecraft-borne measurements of Mg isotopic composition do not have sufficient precision to confirm a solar wind-terrestrial difference in isotopic composition of Mg [5, 6, 7]. The Mg isotopic composition is likely to be uniform in bulk chondrites and planets [8, 9], and by inference in the bulk Sun [1]. The GENESIS mission has directly sampled implanted solar wind in high-purity wafers [10]. The isotopic measurements of Mg in the collected solar wind is challenging for two reasons. The implant solar wind levels are very low for Mg (2×10^{12} atoms/cm²) [10], and the removal of post-crash UTTR contaminants, established to be about a hundred times higher than the solar wind implant [11, 12], needs to be >99.9 %. Determination of the solar wind Mg isotopic composition requires the ability to precisely measure the Mg isotopic composition of picogram quantities of Mg. Here, we report a method developed for low-level Mg isotopic analysis, and some initial results.

Analytical Methods: Measurements of Mg isotopic composition were performed at the Plasma Analytical Facility, Florida State University, on a ThermoFinnigan Neptune™ multicollector ICP-MS equipped with 8 movable and one fixed (axial) faraday cup detectors. An ESI™ Apex nebulizer (80 μl/min) was used for sample introduction. The masses 24, 25, 26 and 27 were simultaneously collected on the L4, L2, Axial, and H2 faraday cups, respectively. There

are no atomic isobaric interferences on Mg or Al. Because of a molecular isobaric interference from CN⁺ on ²⁶Mg⁺, that is significant at these low intensities, we measured all peaks using the high-resolution offset technique [13]. At high-resolution on the Neptune™, the molecular isobar is offset from the atomic peak to higher mass, such that a flat shoulder of the atomic peak is available, and the atomic peak is then measured on the flat portion of the shoulder instead of on the peak center.

We have determined the precision with which Mg isotopic composition could be determined for small quantities of Mg (~10¹² atoms) using 2 ppb (5E13 atoms/ml) and 10 ppb (2.5E14 atoms/ml) reagent Mg standard solutions. These solutions were prepared by dilution with 2% HNO₃ of an in-house 10 ppm Mg solution prepared from high-purity Mg metal for calibration of our ²⁶Mg spike [12]. Figure 1 shows the 2σ relative standard error of the mean (%) as a function of the number of atoms consumed by the measurement using 2 ppb (black) and 10 ppb (red) Mg solutions. Each data point represents a 4-second integration of the beam, and a total of 300 ratios were obtained. The theoretical performance curve is determined by calculating the standard error of the mean of N ratios using the standard deviation of the 300-ratio dataset. The actual performance (crosses) for the test performed here is shown as the cumulative standard deviation divided by the square root of N=2, 3, . . . 300 ratios.

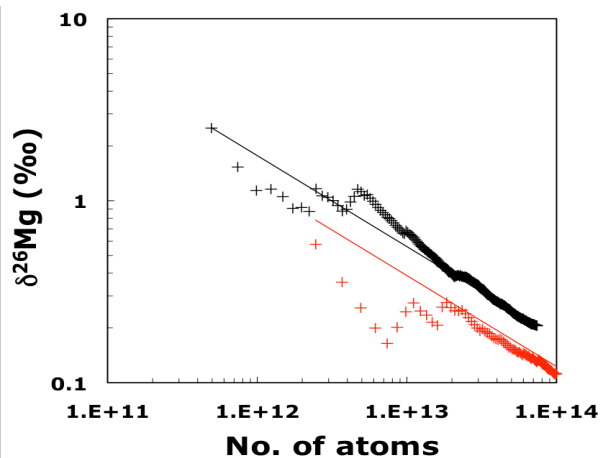


Fig. 1: Cumulative precision obtained as a function of the number of Mg atoms consumed in the analysis of a 2 ppb (black) and a 10 ppb Mg solution (red).

For the 10 ppb ($\sim 2.5E14$ atoms/ml) solution, each ratio consumes $\sim 1.3E12$ atoms, and only 2 ratios are needed to attain a precision of better than 1‰ representing about $2.5E12$ atoms, equivalent to ~ 1 cm² of wafer surface. Mg equivalent to ~ 10 cm² of wafer surface yields a precision better than 0.3 ‰ (20 ratios). The precision currently reported in bulk sample Mg isotopic analysis for $\delta^{26}\text{Mg}$ is about $\pm 0.1\%$ [e.g., 9, 14]. The test results shown in Fig. 1 indicate that $\sim \pm 1\%$ precision in $\delta^{26}\text{Mg}$ is attainable from ~ 1 cm² of wafer fragment. This is sufficient precision to establish whether solar wind Mg is mass fractionated by inefficient coulomb drag effects, and marginally sufficient to establish whether gravitational separation of heavy isotopes has occurred in the Sun [1, 2, 15].

Matrix-matching technique: The isotopic analysis of small quantities of solar wind Mg ($\sim 10^{12}$ atoms) requires modification of the analytical procedures that normally must be applied. For large samples, the Mg is chromatographically separated from the sample matrix and purified to matrix-match the sample Mg with a high-purity reagent standard [e.g., 9]. This introduces several complications: recovery must be complete to avoid isotope fractionation on the column [9], and blanks must be minimized while handling ~ 80 pg of Mg. We adopted a different matrix-matching approach, here. The major matrix impurity in our GENESIS solar wind Mg is Si from the substrate present at levels of ~ 10 ppm Si. To matrix-match our samples and standards we added 10 ppm Si to the standards. This approach works well for very small samples, since it avoids column chemistry (and associated handling blanks). The appropriate standard is then a 10 ppm Si solution with dissolved carbonaceous chondrite adjusted to the same level of Mg concentration as that of the sample.

Results and Discussion: Using 10 ppm Si matrix-matched standards and samples, we analyzed a terrestrial olivine from Kilbourne Hole, Murchison CM2 and Tagish Lake CM1 carbonaceous chondrites, and dirt from the UTTR crash site. All Mg isotopic compositions are normalized to an average of the terrestrial olivine and bulk chondrite isotopic compositions. The results are shown in Fig. 2. The similarity of the terrestrial and chondritic Mg isotopic compositions is consistent with recent studies [8, 9]. The UTTR dirt is isotopically lighter than the bulk chondrites or terrestrial olivine by 0.3 ‰ per amu. Assuming no Mg isotope fractionation occurred during the contamination of the wafers (e.g., vapor deposition during impact heating), UTTR contaminants can be discriminated from solar wind Mg, even if solar wind Mg is identical

in its isotopic composition to chondritic Mg, using about 10^{14} atoms of Mg, or about 100 cm² of wafer. This is a demanding but not impossible task. If solar wind Mg is isotopically distinct from chondritic (or terrestrial) Mg isotopic composition by about 10-20 ‰, then that effect can be discriminated from UTTR contaminants by analyzing the Mg derived from ~ 1 cm² of GENESIS wafer, providing definitive evidence that the recovered Mg is not of terrestrial origin.

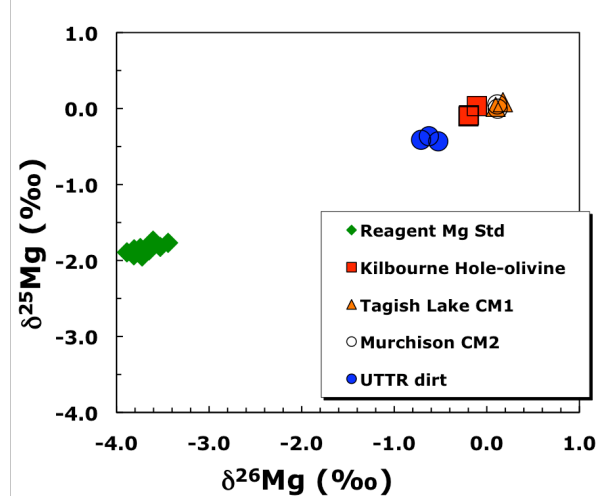


Fig. 2: Isotopic composition of Mg for UTTR dirt (blue), Kilbourne Hole olivine (red), Murchison CM2 (open circle) and Tagish Lake (orange) chondrites, compared with an in-house Mg reagent standard (green).

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