ABUNDANCE OF MANGANESE IN THE SOLAR WIND USING DUAL-IMPLANT CALIBRATION

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Introduction: Of those elemental abundances that are well-measured in the solar photosphere (uncertainties <25%), almost all are consistent within 10% of the abundances in CI meteorites, when normalized to Si. Aside from light elements ($Z < 10$) and the noble gases, only two photospheric abundances differ significantly from the meteoritic values: Mn and Hf[1]. Mn has a photospheric value is ∼26% lower than the meteoritic value. The discrepancy has a statistical significance of 2.6σ. The photospheric measurement, which is complicated by the atomic physics, dominates the uncertainty[2]. If real, the difference could be related to the complex oxidation chemistry of Mn, although it is unclear why other transition metals are apparently not similarly affected [1].

Here we report preliminary measurements of the Mn/Mg ratio and the fluence of Mn in the solar wind. Since the first ionization potential (FIP) of Mn and Mg are nearly identical, the Mn/Mg ratio in the solar wind is likely to be very close to the photospheric value. We used Si collectors returned by the Genesis mission, analyzed by Secondary Ionization Mass Spectrometery, and a novel analytical protocol that uses a dual, high-contrast implant for calibration.

Samples and Methods: The principal challenge of high-precision measurement of SW elemental composition is the development of standards that are measurable in the same profile with the solar wind, using identical beam parameters and detectors. Ion yields vary with primary beam current, so it is important to use identical beam parameters. However the implanted SW has a concentration that is too low for high-precision bulk techniques, particularly ICP-MS. An implant that is large enough to measure by ICP-MS is too large to measure by SIMS using electron multipliers, so must be measured using a Faraday cage, but this is unsuitable for measuring the low-fluence SW. Even if that were not the case, crash-related contamination prevents the use of bulk techniques. Thus, a "bridge" is needed.

Here we created the bridge between high-precision ICP-MS and SIMS measurements using a programmable shutter during ion implantation, to do a dual high-contrast implant. We prepared samples by mounting in an epoxy in an Al round, then ground and polished the samples from the back to avoid crash-related contamination. We did Mn and Mg implants at Kroko, Inc. The implant beam current was set so that the total implant fluence ($\sim 10^{14}$ cm^{-2}) was achieved

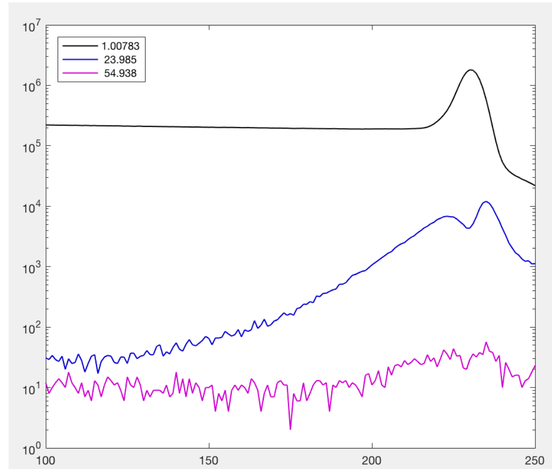

Figure 1: "Detilted" profiles for Mg and Mn. To our knowledge, this is the first observation of solar-wind Mn.

in 2 hours. A set of non-flight Si chips was exposed to the entire fluence. The Genesis Si was exposed behind a shutter, which was programmed to open for a preset time, after the beam was stabilized and the implanter shutter was opened. The shutter, built by one of us (LKTW), is controlled by an Arduino microcontroller, and uses a 1 mm pin as a mechanical feedthrough with Apiezon AP100 (vapor pressure 7×10^{-11} Torr) vacuum grease to maintain a vacuum-tight seal. For this exposure, we programmed the shutter to open for 36 sec, so 0.50% of the total time.

At Kroko, the beam fluence was monitored in real time and displayed on a 4-digit digital display. Because of the mechanical feed-through, the shutter position was visible outside the vacuum chamber. During the exposure, the current and the shutter position were both recorded on cellphone cameras, with audio recording of voices to sync the recordings. The implant flux was stable, but this recording enables us to apply second-order corrections to the fluence ratio. We implanted ^{55}Mn (1.0×10^{14} cm^{-2} at 90 keV) and ^{25}Mg (0.5×10^{14} cm^{-2} at 140 keV).

After implantation, we measured the implant concentrations of the Mn and Mg using ICP-MS. We dissolved the top $\sim 1\mu$m layer of Si chips in a mixture of high-purity hydrofluoric acid (HF) and nitric acid (HNO_3). After dissolution, we evaporated the HF/HNO_3 mixture and redissolved the residue in 1-2 ml dilute HNO_3 for measurement on the Agilent 8800 ICP-MS. In previous analyses, we have demonstrated $2 - 5\%$ (2σ) uncertainties on 1 ppb ^{55}Mn aliquots in analyses of Hayabusa samples. A ^{55}Mn implant with 10^{14}cm^{-2} in 1 cm^2 in 1.5 ml solution corresponds to 6 ppb ^{55}Mn, so this is well within the range for which ICP-MS has demonstrated the required accuracy. Actual blank levels were < 0.1ng. We analyzed two chips. The smaller chip (0.14 cm^2) gave 94% of the nominal Mn implant fluence. The larger chip (0.56 cm^2) gave less than half of that value, which we interpret as incomplete leaching of the Mn implant from the chip. Using the measured fluence ratio, we measured the ion yield of those elements relative to Mg, then derived the SW Mn/^{24}Mg ratio by integrating over the profiles after decontamination and flattening. The Mg blank was too high to make a reliable independent measurement of the implant Mg, so the internal Mn/Mg ratio rests on the assumption that the integrated current measurement at Kroko had the same proportionality for Mn and Mg. The Mn fluence measurement is independent of the Mg implant measurement.

We also analyzed the Genesis chip by SIMS using the ims1280 at Hawai'i, using a O_2^+ primary beam in 40μm $\times$ 40μm rasters in imaging mode. We chose a section of the wedge-shaped Si chip in which the implant was cleanly separated from the solar wind. Because the chip was mounted at a $\sim$0.5° angle, we "detilted" the solar wind profile during analysis. In Fig. 1 we show the H, ^{24}Mg and ^{55}Mn detilted profiles. To our knowledge, this is the first observation of Mn in the solar wind. There are 405 counts in the Mn peak above background, giving a statistical uncertainty of 10% at 2σ.

Using the nominal fluences, we computed the relative ion yield for Mn and Mg, and corrected this to compute the ^{55}Mn/^{24}Mg ratio in the solar wind. We found that ^{55}Mn/^{24}Mg $= (8.8 \pm 0.9) \times 10^{-3}(2\sigma)$. This value is about 23% lower than the recommended CI value, 11.4×10^{-3}, and differs from it by 2.9σ. The measurement is within 1σ more consistent with the measured photospheric value, 8.4×10^{-3}. We caution, however, that this result is uncalibrated by ICP-MS, due to the large Mg blank. We think that this large blank is due to contamination in the reagent, so it should be correctable in the future. We also found significant contamination in Co, Cr, Fe, Ti, which may have originated from stainless steel tweezers used for handling the chips. The ICP-calibrated fluence of Mn in BC-array Genesis chips is $(5.9 \pm 0.6) \times 10^9$ cm$^{-2}(2\sigma)$. Normalization to the independently-measured BC-array Mg fluence, $(1.68 \pm 0.03) \times 10^{12}$ (Burnett, private comm.), gives ^{55}Mn/^{24}Mg $= (9.0 \pm 0.9) \times 10^{-3}(2\sigma)$, in agreement with the internally-measured ratio.

Aside from measurements of noble gases, no elemental ratio measurement in Genesis samples has yet met the initial promise of the Genesis mission, which was to measure elemental ratios to better than 10% at 2σ.

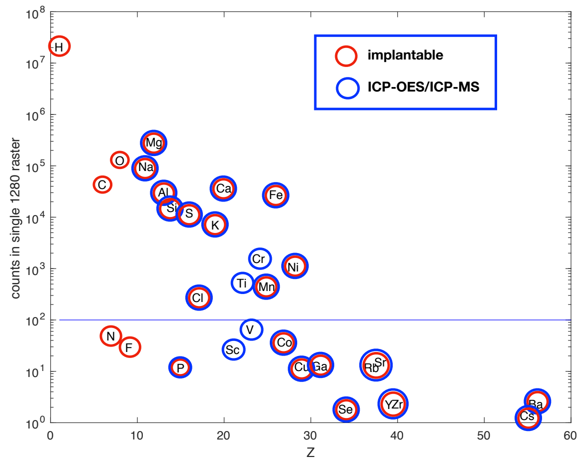

Figure 2: Expected solar wind statistics in a single ims1280 40μm by 40μm raster (left) plotted against atomic number and (right) against FIP. The statistics are based on observed SW profiles for Mn (positive ions N, Na-Ge, Rb-Zr; O_2^+ primary beam) and S (negative ions C, O, F, P, S, Cl, Se; Cs^+ primary beam), with RSFs from [3]. Analyzable elements by ICP-OES or ICP-MS are circled in blue. Elements that can be implanted by Kroko, Inc. are circled in red. All elements shown can be analyzed by ims1280.

This technique shows promise for high-precision measurements of many other elements. Indeed, Mn may be the most challenging, at least in the statistical sense. Using the observed counting statistics for single depth profiles in Mg, we estimated counting statistics for other elements. We used the RSF values from [3] and cosmic abundances from [4], but did not include any FIP-dependent SW abundance effects, which lower statistics by a factor of $\sim$3 for high-FIP elements. Ten elements (Na, Mg, Al, S, Cl, K, Ca, Mn, Fe and Ni) have been implanted successfully by Kroko, are in principle analyzable by ICP-MS, and will have at least 100 counts in a single SIMS profile. Mn has the lowest statistics in a single profile, $\sim$400 counts above background. This gives $\sim$10% (2σ) statistical precision in a single profile. Achieving 5% (2σ) will require four profiles. Most other elements will achieve this statistical power in a single profile, although we plan to carry out more to assess consistency (Fig. 2).

References: [1] Palme H. *et al.* (2014) in *Planets, Asteroids, Comets and the Solar System* (edited by A. M. Davis),Vol 2., *Treatise on Geochemistry*, 15 [2] Blackwell-Whitehead R. *et al.* (2011) A&A 525, 44 [3] Wilson, R. G. (1995) Int. J. Mass Spectrometry. Ion Proc., **143**, 43 [4] Lodders K. & Fegley B. (1998) The Planetary Scientist's Companion [5] Burnett D. S. *et al.* MAPS in press.