TOWARDS THE ISOTOPIC MEASUREMENT OF SOLAR WIND CARBON IN THE GENESIS SILICON TARGET. A. B. Verchovsky, S. Sestak and I. A. Franchi, Planetary and Space Sciences Research Institute, Open University, Milton Keynes, MK7 6AA, UK. E-mail: a.verchovsky@open.ac.uk.

Introduction: Measurement of the solar wind carbon isotopic composition involves the analysis of a pure Silicon (Si) target exposed to the solar wind, without concentration, on the Genesis spacecraft [1]. The total carbon flux is expected to be of the order of $\approx 1ng$ C per $10cm^2$ target. This is a very small quantity even for a static mode mass spectrometry (see below), and therefore, the measurement represents a challenging task. The critical aspects which need to be addressed for successful measurement are: (1) system blank and (2) surface contamination of the target material by carbon containing species.

Analytical techniques: A static mode carbon isotope analysis technique was developed at The Open University about 20 years ago [2]. Despite the elapsed time, the instrument still remains one of the most sensitive techniques used for carbon isotope analyses. It allows the measurement of sub-nanogram quantities of carbon with a precision of ~1‰. The current instrument has been improved by progressive modification of the extraction and purification systems and by computer automation of all the stages of analysis. The former helped to promote a reduction in the blank level while the latter assisted in better reproducibility of the results. In particular the system is now made completely of stainless steel metal with the exception of the quartz combustion tube and glass cold fingers for collecting of carbon dioxide (CO_2). The combustion tube is surrounded with an outer alumina tube with the annular space between the tubes being pumped to a low vacuum in order to prevent the collapse of the inner quartz tube at high ($>1300^oC$) temperatures provided by a tube furnace with a SiC heating element (maximum T=1500^oC). Aliquots of CO_2 are measured using a high sensitivity baratron and are controlled at the same time by the intensity of the mass 44 peak since the influence of other gases , e.g. H_2, becomes an important factor at the nanogram level.

System blank: The solar wind carbon implanted into the Si target is released in the form of CO_2 by oxidation of the Si substrate in an oxygen atmosphere. Only a thin surface layer about 100 nm needs to be oxidized in order to extract the implanted carbon. However it is known that effective oxidation of Si only occurs at high temperatures (1000 to 1400^oC). This determined the conditions at which an appropriate blank level needed to be achieved.

It was determined that the most important sources of C blank were due to the high temperature furnace (1-2 ng depending on temperature) and CuO (~3 ng), a common source of oxygen. The rest of the vacuum system contributed sub-nanogram amounts of C. Carbon from CuO was mostly released at high (850^oC) temperatures. The significant C blank from the CuO made us develop a different way of supplying oxygen into the combustion section and removing it from the section at the end of combustion. High purity compressed oxygen gas was used which was additionally cleaned using repeated sorption-desorption procedures on molecular sieves. Separation of the CO_2, formed during combustion, from the residual oxygen was performed with the help of a glass fibre filter at liquid nitrogen temperature. The CO_2-O_2 mixture is slowly pumped through the filter and almost 100% of CO_2 is trapped by it. Subsequent warming of the filter to 50-100^oC quantitatively liberates the trapped CO_2. A similar CO_2 trap was used to analyse atmospheric CO_2 [3]. In terms of C blank this system is a factor of ~6 better than the earlier CuO system.

Only after incorporating the new oxygen supply system described above, we were then able to investigate the furnace blank. The furnace blank is strongly temperature-dependent (Fig. 1), rising steeply above 1000^oC. We believe that one major source is the quartz combustion tube material in which carbon was introduced during its manufacture. Most of the carbon can be released during initial outgassing of a new tube by baking it out in the presence of oxygen. Following this initial period of time (2-3 days), the residual carbon level diminishes at a much slower rate and reaches an almost stabilized level (1-2 ng).

Influence of hydrogen: During analysis, a small amount of hydrogen (H_2) was always present along with CO_2 even after purification of the latter. The origin of the H_2 is from outgassaing of the metal parts of the vacuum system and its amount is proportional to the time the system vacuum sections are kept closed without pumping. On introduction into the ion source of the mass spectrometer the H_2 causes protonation of CO_2 molecules due to ion-molecular reactions forming CO_2H, this in turn, changes the measured isotope ratios especially for the $^{45}M/^{44}M$. In order to reduce this effect, an additional cold trap was incorporated into the inlet system where the ready-to-measure CO_2 is

quickly (<2 minutes before mass spectrometric measurement) cryogenically separated from the hydrogen.

^{13}C implanted in Si : A Si target, analogous to that exposed to the solar wind during the Genesis mission, was implanted with ^{13}C and ^{36}Ar at Los Alamos National Laboratory (LANL) with implantation energies similar to those for the solar wind and with a total fluence of 5×10^{14} and 1×10^{13} cm^{-2} respectively. The samples were analysed in our system in order to determine the required temperature and extraction efficiency for the release of the implanted carbon by combustion. A stepped heating program was utilised. In a number of early experiments, a bimodal release of the implanted ^{13}C was observed (Fig. 2). Such a complicated release profile appears to be the result of several processes that control the release: (1) progressive oxidation of Si from the surface to the interior of the sample; (2) diffusion of sub-surface implanted carbon atoms in the original Si both towards the surface and bulk Si wafer volume and in the SiO_2 oxide layer to the surface and (3) oxidation of the carbon atoms that have migrated to the oxygen/sample surface interface into CO_2. It is postulated that the difference in the diffusion rates of carbon in Si and in the formed SiO_2 have the greatest affect on the ^{13}C release profile. The implanted ^{13}C release temperature (from 1000 to 1400ºC) is high enough to provide an effective discrimination technique from any terrestrial organic contamination with typical combustion temperatures in the range 300-700ºC. However the high temperature release, on the other hand, is also associated with a higher blank level.

An additional surface pre-cleaning technique trialed initially at the OU of UV/Ozone cleaning has been found to clean carbon contamination to levels below non-flight standards [4]. This pre-cleaning step reduces the surface C contamination load to the combustion tube.

For 10 irradiated samples, the average yield of recovered carbon was 40±15%. This appeared to be due to incomplete oxidation of implanted carbon atoms. One of the possibilities to improve the carbon yield was to use a Pt metal catalyst. In order to test the effect of Pt on the release of ^{13}C we analysed an irradiated sample wrapped in Pt foil. The result of such analyses not only showed the recovered yield to be almost 100%, but also that the ^{13}C release profile became a single peak at a lower temperature. The exact cause of this effect remains to be determined – but may be the result of enhanced oxidation of the Si via the production of excited oxygen atoms on the Pt surface or from direct reaction of the Pt with the Si to form one of a number of possible Pt-Si phases. The new formed metal may oxidize more readily or have higher diffusion rates of C and/or O than the Si metal.

The modified release temperature of the implanted C has two immediate benefits for the Genesis analyses. The release temperature is moved to lower temperatures where lower system blanks can be attained and the sharper release means that the solar wind C can be released with fewer steps. Both effects enhance the sample to blank ratio. With first signs of implant not appearing before 800˚C quantitative removal of surface contamination can still be readily achieved.

Summary: Modification of the static mass spectrometer system and introduction of Pt foil to the sample combustion environment have significantly reduced the blank associated with extraction of solar wind implanted C in Si wafer.

References: [1] Burnett D. S. et al. Space Sci. Rev. (2003) 105, 509; [2] Wright I. P. and Pillinger C. T.(1989) US Geol. Bull. 7890, 9; [3] Brenninkmeijer C. A. M and Rockmann T.(1996) Anal. Chem. 68, 3050; [4] Sestak, S. et al. (2006) LPSC XXXVII, Abstract # 1878.
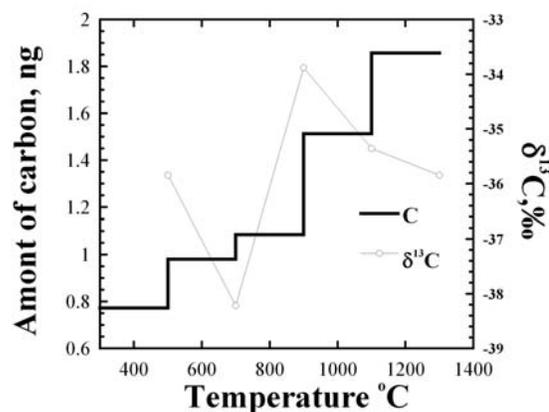

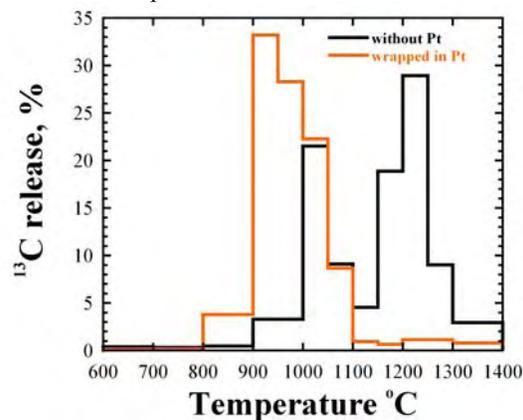Figure 1. Typical system blank as a function of the furnace temperature.

Figure 2. Effect of Pt on the release of ^{13}C from the irradiated Si.