SOLAR WIND SAMPLE RETURN FROM GENESIS: TOWARDS THE EXTRACTION AND ISOTOPE RATIO MEASUREMENT OF NANOGRAM QUANTITIES OF OXYGEN IMPLANTED INTO DIAMOND. A. L. Butterworth, I. A. Franchi and C. T. Pillinger, Planetary Sciences Research Institute, The Open University, Walton Hall, Milton Keynes MK7 6AA, UK.

Introduction: Genesis is a NASA Discovery mission aimed at determining the elemental and isotopic composition of the sun through measurement of the solar wind. The calculated values should be of a high precision so as to be comparable with data collected from other planetary material. The means to accomplish sensitive, accurate and very precise isotopic measurements is to analyze material in a specialised terrestrial laboratory, thereby requiring a sample return mission. The Genesis spacecraft is due for launch in 2001, when it will be inserted into a Lassajou orbit at the libration point L1. Arrays of collector material will be deployed so that solar wind ions will be implanted into the collectors over the two-year collection period. The spacecraft will then be returned to Earth in 2003.

The top priority aim of the mission is to determine the ratio of solar ^{16}O, ^{17}O and ^{18}O isotopes compared to a terrestrial standard with a precision of 0.1 %. To this end, an electrostatic concentrator [1] with a 6 cm diameter target has been developed to satisfy the sample requirements for oxygen analysis, providing a twenty-fold increase on the tenuous solar wind fluence at 1 AU. The returned sample available for analysis is expected to be ~5 nanograms of bulk solar wind oxygen implanted per cm^2 surface area.

This work addresses the technical challenges to be addressed in order to analyze the small solar wind oxygen samples for precise isotopic composition measurements. The issues are (1) the analytical instrumentation in terms of sensitivity and precision, and (2) the extraction of oxygen from its collector material without isotopic fractionation.

Considering first the prospect of analyzing 10 ng oxygen, typical oxygen isotope analyses are performed on a few to tens of micromoles of O_2 gas, although it is possible to work to somewhat smaller sample sizes at the expense of precision [2] Analysis of the Genesis samples will require a considerable reduction of the current smallest sample sizes, but will allow some leeway on the best analytical precision.

For the extraction of implanted ions, UV laser ablation of the collector material offers a practicable solution [3]. However, the technique must be able to differentiate between the solar wind sample and terrestrial oxygen contamination. This point alone has directed much of the pre-flight development of the Genesis Science Team. The chosen collector material must have an exceptionally high bulk purity (limits set at 1 % of expected solar wind sample level) and be suitable for UV extraction as well as satisfying a variety of spacecraft related properties. Synthetic diamond has been proposed as the most suitable material.

An unavoidable concern of a sample return mission is the surface contamination of the collector by terrestrial oxygen containing species. An extraction procedure must therefore offer "depth sensitivity", or a means of separating this contamination from the implanted sample. Oxygen ions are expected to be implanted to a range of depths over several hundred angstroms, but contamination is expected to be limited to the very surface.

Method: A laser extraction system was built for a carbon extraction system [4], also intended for Genesis returned sample analysis. The system was modified to become a dedicated oxygen extraction system. The main components included a Nd/Yag Laser with frequency doubling to produce a 266 nm beam. A computer-controlled x-y stage allowed accurate rastering of the sample under the fixed UV beam in a stainless steel sample chamber with UV grade quartz windows placed top and bottom. The assembly allows any unabsorbed beam to pass through the chamber, minimizing effects from the chamber itself. Inside, a perforated disc acts as a sample support for diamond wafer test samples.

The chamber was attached to a Pyrex vacuum line and evacuated to a pressure of 10^{-6} mbar. When a 10 Hz pulsed laser beam was rastered over diamond implanted with oxygen, a mixture of CO and CO_2 were released. The vacuum line included the means for trapping CO_2 (cryogenic trap) and CO (molecular sieve at –196 °C). With contamination very much the central issue, levels of CO and CO_2 collected in the appropriate manner without lasing diamond were as low as 0.1 ng oxygen as either species.

Oxygen isotope ratio determination. The gas recovered from laser extraction was expected to be CO and CO_2. There was the opportunity to utilize a laser fluorination technique to liberate an oxygen gas analyte for subsequent isotope ratio determination. However, the technique remains to be developed, particularly in terms of reagent blank and gas analysis of nanogram quantities of oxygen. An alternative route was to limit chemical processing and analyze the CO, CO_2, or both to determine the oxygen isotope ratio.

Static mass spectrometry is a technique which can be used for analyzing picomole quantities of CO and CO_2 for carbon isotope ratio measurements [5]. It has

been investigated here as to whether the technique might be developed further to allow oxygen isotope measurements on these analytes. Oxygen itself is not a suitable analyte for static mass spectrometry due to the prohibitively short lifetime of the gas in the presence of the hot filament in an electron impact ionization source.

For isotope ratios to be determined in a static mass spectrometer (MS), the analyte must survive long enough to allow measurement of sufficient ions to obtain a statistically meaningful ratio. CO_2 has a half-life of approximately 1 minute, but CO survives much longer. In addition, isotopic exchange or fractionation should be minimal, or at least well understood if it does occur. Tungsten or coated-W filaments ubiquitous in MS sources were unsuitable for use in a static oxygen isotope analyzer, because rapid isotopic exchange effectively wiped out the oxygen isotopic signature of the analyte. A search has been made to find an alternative filament material.

A mass spectrometer was already attached to the vacuum line described above, from where reference gases were admitted to the instrument. Various filaments were used in an otherwise unchanged MS source and ^{18}O enriched and depleted CO_2 gases were prepared and analyzed.

Choice of collector material. Two types of diamond were tested in the system for their suitability for laser extraction and in particular for the possibility of depth sensitivity. A sample of CVD (chemical vapour deposition) diamond implanted with ^{18}O was analyzed using laser extraction and the online static MS with Re filament (see below). The laser beam was rastered over the diamond in 50 micron strips ablating a total area of 1 mm^2. The same area was rastered and gases yielded were analyzed in the same way. The presence of the minor isotope ^{18}O measured as CO in relatively large quantities allowed a depth profile in the diamond to be marked out.

A second proposed collector was a thin film of amorphous diamond on a silicon substrate. Again, Genesis pre-flight testing material was evaluated in the system in the same way as described for CVD diamond using an ^{18}O-implanted amorphous diamond sample.

Results: By testing several different filaments, rhenium was found to be a suitable filament for use in the MS source. Oxygen exchange was observed, but over a time scale of several minutes. Preliminary analyses of isotopically distinct CO_2 gases were hardly precise, but certainly were sufficient to allow testing of the proposed oxygen collector materials.

Polished CVD diamond did not readily couple with the 266 nm beam, but radiation-damaged diamond was very effective. Fortunately, all returned samples will be heavily radiation damaged due to the relatively high helium fluence on the Genesis concentrator. Pristine and radiation damaged amorphous diamond coupled equally well with the UV laser.

Complete extraction of the implanted ^{18}O from 1mm^2 area of either amorphous or CVD diamond was expected to yield 0.8 ng ^{18}O. The table below indicates the excess of ^{18}O obtained during rasters over the same 1mm^2 area using different beam energies; layers are numbered from the surface down.

Diamond, layer	Energy mJ/pulse	CO excess ^{18}O, ng
CVD, 1	0.2	0
CVD, 2	2.9	0.34
CVD, 3	2.9	0.09
Amorph, 1	0.2	0
Amorph, 2	2.9	0.22

Lower energy surface rasters yielded some terrestrial O, but a subsequent higher energy raster over the same area yielded more CO as a mixture of terrestrial O plus the implanted ^{18}O. The CVD profile showed that the amount of excess ^{18}O peaked at the second raster. The yield of implanted ^{18}O was roughly one half of that expected, indicating that much improvement is required.

Further development of the laser extraction system will focus on minimizing "blank" CO and CO_2 yielded during the lasing step and further improving the depth sensitivity and sample yield. For example, further depth resolution is possible by fine-tuning of the UV beam energy.

The use of rhenium as a MS source filament has shown that it may be possible to measure the ratio of the three stable oxygen isotopes in a static mass spectrometer, using CO as the analyte. The use of static mass spectrometry immediately offers the increase in sensitivity required in order to analyze 10 ng oxygen solar wind samples and a new generation of MS capable of high precision O measurements at this sample size is under development.

References: [1] Burnett D. S. et al. (1997) GENESIS Feasibility Study. [2] Young et al (1998) *GCA*, 62, 3087-3094. [3] Young et al. (1998) *GCA*, 62, 3161-6168 [4] Butterworth A. L. et al. (1999) *LPS XXX*, Abstract #1796. [5] Prosser S. J. (1990) *Chem. Geol.* 83, 71-88